Development of pyrolysis process models for the production of lignin based phenols using Aspen Plus®

by

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ABSTRACT

Lignin is an abundant organic solid waste presently produced in the form of black liquors from the paper and pulp industry, and is expected to be produced from lignocellulose biorefineries via chemical/biochemical processes for implementation in the sugar industry in fore sable future. Unlike various other organic wastes, lignin is made of chemical compounds called phenols, which have a relatively high market values (i.e. US$1500 – 12 000 per tonne), and can be produced from lignin residues by pyrolysis.

In order to determine the techno economics of extracting phenols from lignin, this robust catalytic pyrolysis of lignin Aspen Plus® models were developed in this study.. Four scenarios were developed and results of the models were compared against each other to determine the most economically viable process of producing phenols from lignin. Scenarios 1 and 2 were about producing a crude phenolic mixture called creosote via catalytic pyrolysis of lignin, whilst scenarios 3 and 4 were about producing phenolic fractions from the lignin via catalytic pyrolysis and fractional distillation. Scenarios 1 and 3 used a relatively cheap catalyst sodium hydroxide, whilst scenarios 2 and 4 use relatively expensive catalyst zeolite.

The technical performance analysis showed that scenarios 1 and 2 performed better, as they were found to be energy self-sufficient as the energy generated in combustion of char was able to meet the energy demands of the plants. Unlike scenarios 1 and 2, scenario 3 and 4 were found to need imported energy so as to meet the energy demands of the plants. The economic analysis showed that scenario 3 and 4 had the highest IRR values of 19.27% and 18.23% respectively. Production of crude phenolic solution (creosote) had generated the lowest IRR where scenarios 1 and 2 had IRR values of 1.10% and 2.07% respectively. Both scenario 3 and 4 showed it was more economically viable to produce phenolic fractions from lignin but is was found to be economically feasible to produce a phenolic mixture using a cheap catalyst as evidenced by the IRR of scenario 3. Production of phenolic fractions from pyrolysis of lignin using a catalyst of high market value (i.e. scenario 3) was economically viable

but it was lower than scenario 3 which generated additional sales revenue through selling the by-product sodium oxide. The environmental impact analysis (CO_2 emissions) showed that all four scenarios emitted less CO_2 than fossil based phenols (4.5 kg CO_2 per kg phenol). Comparison of the CO_2 emissions of the four scenarios showed that scenario 4 emitted the highest CO_2 emissions (2.72 kg CO_2 per kg phenol) whilst scenario 1 was found to emit the least CO_2 emissions (1.80 kg CO_2 per kg phenol). Thus it can be concluded that production of phenolic fractions from lignin was preferred economically viable route but the yields of the phenolic compounds have to increase above the current 1wt % of lignin so as to increase the productivity of the phenolic fractions that will in turn increase the IRR thus attracting more investment.

OPSOMMING

Lignien is 'n oorvloedige organiese vaste afval wat tans geproduseer word in die vorm van swart drank van die papier en pulp nywerheid, en wat verwag word om van lignosellulose biorefineries te produseer via chemiese / biochemiese prosesse vir implementering in die suikerbedryf in die toekoms. Dit word tans verbrand in die ketels om stoom en elektrisiteit vir die papier en pulp nywerhede te genereer. Maar lignien het ook potensiaal om in chemikalieë op toegevoegde waarde omskep te word, met die doel om die ekonomiese lewensvatbaarheid van biorefineries te verbeter. In teenstelling met verskeie ander organiese afval, is lignien gemaak van chemiese verbindings genoem fenole, wat 'n relatief hoë markwaardes (dit wil sê VSA $ 1500 - 12 000 per ton) het, en kan geproduseer word van lignien residue deur pirolise.

. Ten einde om die tegno-ekonomie van fenole vanaf lignien te bepaal, robuuste katalitiese pirolise van lignien Aspen Plus model in hierdie studie ontwikkel. Vier senario's was ontwikkel en die resultate van die modelle is vergelyk teen mekaar om die mees ekonomiese lewensvatbare proses van die vervaardiging van fenole van lignien te bepaal. Senario's 1 en 2 was oor die vervaardiging van 'n ruwe fenoliese mengsel genoem kreosoot via katalitiese pirolise van lignien, terwyl senario 3 en 4 oor die vervaardiging van fenoliese breuke van die lignien via katalitiese pirolise en fraksionele distillasie was. Senario's 1 en 3 gebruik 'n relatief goedkoop katalisator, terwyl senario 2 en 4 gebruik relatief duur katalisator zeoliet.

Die tegniese prestasie analise het getoon dat senario 1 en 2 beter presteer, terwyl hulle besig was gevind om energie selfonderhoudend te wees as die energie wat in verbranding van char in staat was om die energie behoeftes van die plante te ontmoet. In teenstelling met senario's 1 en 2, senario 3 en 4 is bevind dat ingevoerde energie benodig word om die energie behoeftes van die plante te ontmoet..

Die ekonomiese aanwysers was bepaal deur kontantvloei afslag deur die bepaling van die IRR vir die vier senario's gebaseer op die markpryse van die fenoliese breuke en 'n paar ekonomiese aannames. Die ekonomiese ontleder het getoon dat senario 3 en 4

die hoogste IRR waardes van 19.27% en 18.23% onderskeidelik het. Produksie van ru fenoliese oplossing (kreosoot) het die laagste IRR waar senario 1 en 2 IRR waardes van 1.1% en 2.7% onderskeidelik gegenereer het. Beide senario 3 en 4 het getoon dat dit meer ekonomies lewensvatbaar te fenoliese breuke van lignien geproduseer het, maar dit was gevind om ekonomies lewensvatbaar te wees om 'n fenoliese mengsel te produseer met behulp van 'n goedkoop katalisator soos blyk uit die IRR van senario 3. Produksie van fenoliese breuke van pirolise van lignien met behulp van 'n katalisator van hoë markwaarde was ekonomies lewensvatbaar as dit 'n IRR van 18.23% produseer, maar dit was laer as senario 3 wat bykomende omset gegenereer het deur die verkoop van die neweproduk Natriumoksied. Die impak analise omgewing (CO_2 emissies) het getoon dat al vier senario's uitgestraal meisie CO_2 as fossiel gebaseer fenole (4.5 kg CO_2 per kg fenole). Vergelyking van die CO_2 emissies van die vier senario's het getoon dat senario 4 (2.72 kg CO_2 per kg fenole) die hoogste CO_2 uitgestraal het terwyl senario 1 (1.80 kg CO_2 per kg fenole) die minste CO_2 vrygestel het.So dit kan afgelei word dat die produksie van fenoliese breuke van lignien verkies was om ekonomies lewensvatbare roete maar die opbrengste van die fenoliese verbindings te verhoog bo die huidige 1wt% lignien ten einde die produktiwiteit van die fenoliese breuke wat op sy beurt die IRR sal toeneem verhoog dus lok meer beleggings.

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NOMENCLATURE

US$ per tonne - US Dollar per tonne

NVP - Net Present Value

Bar - 10^5 Pascal

CAPEX - Capital Expenditure

CHP - Combined Heat and Power

IRR - Internal rate of return

CO_2.e – Carbon Dioxide equivalent

TAS – Total Annual Sales

MW - Mega Watts

kJ - kilo joules

OPEX - Operating Expenditure

HHV - Higher Heating Value

TCI - Total Capital Investment

MWh – Mega Watt Hour

CHAPTER 1

INTRODUCTION

1.1 Background Study

Usage of fossil based resources has becomes significantly unjustifiable as effects of global warming become more evident [1]. Hence the need for the development of renewable resources so as to replace fossil based resources. [2]. But the maturity of fossil based technologies that enable production of cheap products is currently hindering commercial maturity of the majority of bio based processes [3]. Another reason why renewable resource based products from biomass are not economically viable is the recent drop in crude oil price (i.e. dropped to US$27 per barrel as of January 2015) [4] [5]. However production of chemicals from renewable plant has the potential to be economically viable in the near future due to abundance of the cheap biomass [2][3]. In order to improve the performance of bio based process, a bio-refinery approach based on an optimal use of all the by-products is required [6]. In particular, conversion of lignin (a residue produced in abundance in biorefineries) into value added chemicals has the potential to be improve the sustainability and economic viability of biorefineries [7][8].

Lignin is an organic polymer that is composed of phenolic monomers. These phenolic compounds have relatively high market value in the range US$1 500 - 13 000 per tonne [9][10]. Phenols have various applications in the motor and electronic industries where they are mainly used to make high tensile strength materials [11][12]. Since these industries continue to have high annual growth rates [13], the economic viability of producing phenols from lignin is worth investigating. Lignin is an abundant organic solid polymer presently produced in black liquors from the paper and pulp industry, and is expected to be produced from lignocellulose biorefineries under investigation for future implementation in the sugar industry. It is currently being burnt in the boilers to generate steam and electricity for the paper and pulp industries.

1.2 Research proposal

1.2.1 Motivation

Lignocellulose based biorefinery focussing on carbohydrate conversion, produce abundant quantities of lignin residue that is currently is being utilised only for energy generation purposes [14]. In the biorefinery, the pre-treatment of lignocellulose is a highly energy intensive process that is derailing the economic viability and sustainability of the bio-refinery [15]. But conversion of the lignocellulose residues into value added chemicals (i.e. phenols, bio-ethanol, etc.) will improve the economic viability of the biorefinery and also add much needed cash into industries such as Sugar Mills, Pulp and paper mills through annexing a lignocellulose biorefinery onto the these mills [16][17]. But for residual lignin to be made available in the biorefinery, the energy efficiency of the sugar mills needs to be first improved so that there is residual bagasse lignin available for conversion [18]. The feedstock to the biorefinery can be increased by importing green cane harvests and harvest residues that can be fed as a combined stream into the biorefinery so as to produce lignin that can be converted into value added chemicals [18]. Advances in research of biomass conversion technologies such as pyrolysis have shown it is possible to convert lignin to value added chemicals such as phenols [9][19]. Thus investigation of the economic viability of converting lignin into phenols using biomass conversion technologies is essential for sustainable production of bio-phenols. This is only possible through development of robust models considering economic viability and level of environmental impact.

1.2.2 Research questions

In this study the main objective was to investigate the economical worthiness of converting lignin into value added chemicals via catalytic pyrolysis than just combusting it in boilers? Specifically:

1. What type of catalyst can economically improve the pyrolysis conversion of lignin into phenols?

2. What are the optimal pyrolysis conditions necessary for the production of phenols from lignin?

3. What type of phenols can be economically produced from lignin?

4. What are the maximum phenol yields that can be produced from lignin pyrolysis?

5. Which lignin based phenols have the higher potential to penetrate the phenol market which is currently dominated by fossil based phenols?

6. Is it environmentally friendly to produce bio-phenols as compared to producing fossil based phenols?

7. What are the environmental and economic impacts of producing phenols from lignin?

1.2.3 Objectives

For this study, the main objectives were to first develop robust process models that could accurately predict the product spectra (i.e. phenols) of lignin conversion technologies (specifically pyrolysis and fractional distillation of pyrolysis products). Thereafter compare the various bio-phenol production scenarios so as to determine the desired economic viable route and its environmental effects. Specifically the objectives were as follows:

1. Simulate different steps of the lignin conversion into a crude phenolic mixture process routes via catalytic pyrolysis and thereafter fractionate the crude phenolic mixture into phenolic fractions.
2. Maximise the yields of targeted phenolic compounds
3. Determine the costs associated with each developed models such as CAPEX, OPEX so as to determine the economic viability of each process route.
4. Determine the carbon footprint over the life cycle of sugarcane cultivation and conversion of each scenario so as to determine the environmental impact of each process route.

1.2.4 Impact of study

The following specific outcomes are expected from the implementation of this study;

1. The economic viability of second generation biorefineries is currently being hindered by the high energy consumption during pre-treatment of biomass and

the low selling prices of bio-products. Thus if phenol production is proven to be economically feasible, the potential of second generation technologies to be economically viable will improve.

2. Economic viability of phenol production from lignin can benefit local communities through job creation.
3. Penetration of bio-phenols into the phenol market will provide a greater drive for promotion of green based processes.

1.3 Thesis layout

Figure 1 shows the layout of the thesis as to how different chapters integrate with each other. Chapter one delves into the introduction about the background, objectives and expected impact of this study. Chapter two gives in depth literature study of lignin conversion technologies, with particular attention being given to pyrolysis, phenol fractionation technologies, economic analysis of bio-refineries and environmental impact analysis. This chapter goes further by discussing lignin chemistry, composition of phenols obtained from lignin and markets of such phenols. Chapter three describes four scenarios of producing phenolic compounds from lignin via catalytic pyrolysis and fractional distillation. It also gives an in-depth approach and methods of modelling lignin pyrolysis and challenges associated with modelling lignin catalytic pyrolysis. Chapter four discusses the results of the process, economic and environmental impact analysis of the four scenarios of producing phenolic compounds from lignin. The interpretation goes on further to compare various technologies based on economic parameters and greenhouse emissions results. Chapter five summarises the thesis by discussing the conclusions and recommendations.

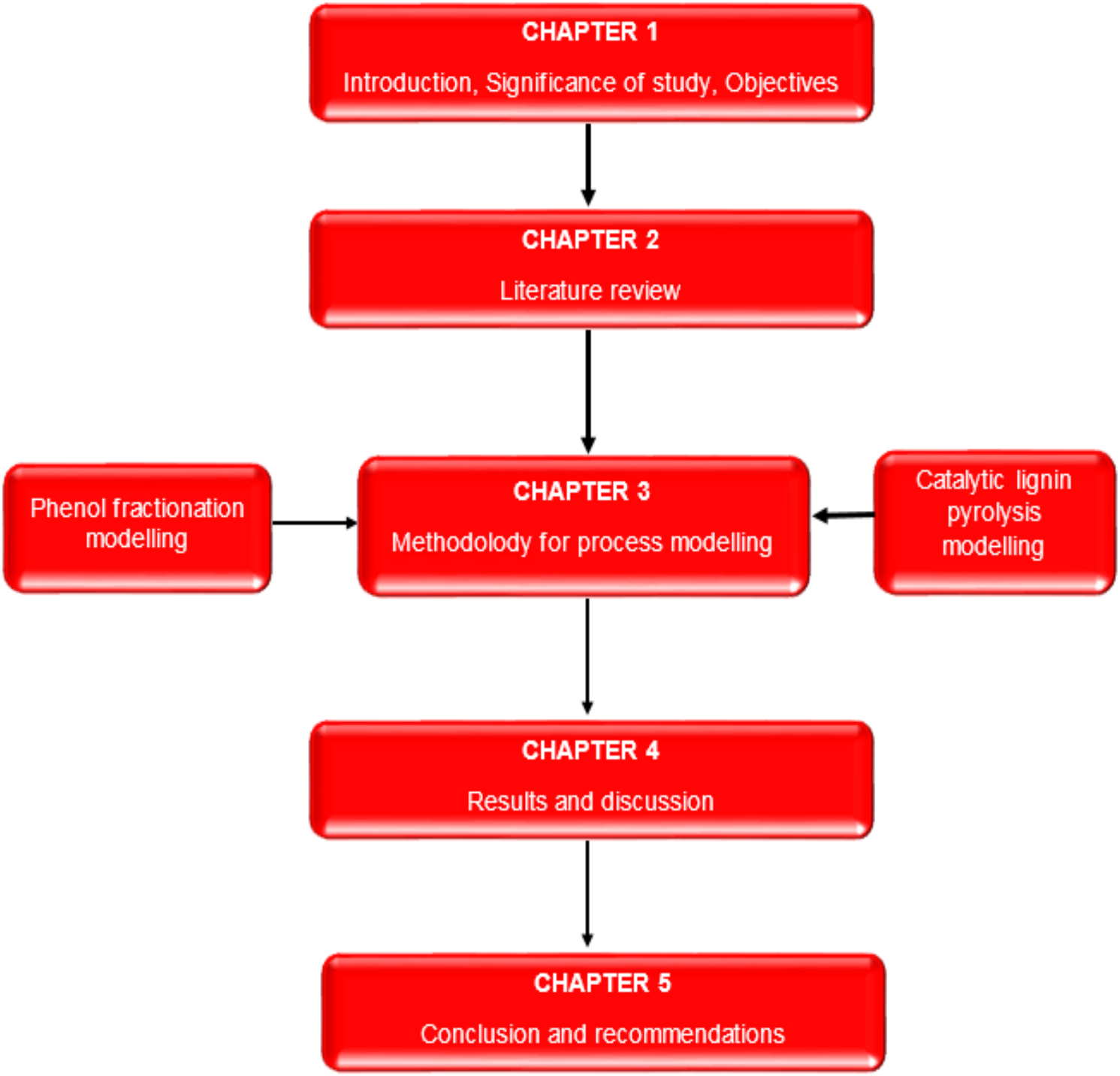


Figure 1 Flow diagram of thesis layout

CHAPTER 2

Literature review

2.1 Introduction

Lignocellulosic biomass is an abundant cheap plant material that is available in nature that is mainly composed of lignin (15-35 wt.% mass), cellulose (20 – 45 wt.% mass) and hemicellulose (25-40 wt.% mass) [20][21][22] [23][24]. Global annual production of lignocellulosic biomass is on average is $1 \times 10^{10} – 3 \times 10^{11}$ metric tons [13]. Lignin is the fibrous polymer that gives lignocellulosic plant materials strength against external forces [21]. In the bio-refinery approach that relies on chemical/biochemical conversions, cellulose and hemicellulose are frequently hydrolysed into sugars or biopolymers, whilst the insoluble lignin is typically sent to the boilers to generate steam and electricity for the bio-refinery [25][26].

Lignin has a wide range of applications in various industries such as construction, food, moulding etc. [13][21]. It used to make adhesives, resins, moulding materials, food additives etc.[9] Alternatively lignin can be depolymerised into value added chemicals such as bio-based phenols that have a high market value and wider applications in various industries (i.e. US$1500 – 12 000 per ton) [13][27]. The global phenol industry continues to grow by 4.5 % as of the third quarter of year 2015 [13][28]. Borregaard LignoTech currently dominates the global sales of lignosulphonate products that are made from lignin [1][16]. The other major global player of the lignin industry is Georgia Pacific that produces 200,000 tonnes of lignosulphonates each year [29][30].

2.2 Lignin

Lignin is a complex, amorphous, organic polymer, with a chemical structure that results in classification as a multi-phenolic substance [9][21]. It is composed of three different monomers called hydroxyphenylpropane (H), guaiacylpropane (G), and syringylpropane (S) units, as presented in Table 1 [20][31][22]. Based on the source of biomass, lignin can be classified into three main groups namely hardwood, softwood and non-woody [24] [32]. Hardwood lignin contains both guaiacylpropane

and syringylpropane with a G/S ratio from 4:1 to 1:2, whilst the p-hydroxyphenylpropane has the least content [33]. Softwood lignin contains mainly guaiacylpropane (90 – 95%) and low levels of hydroxyphenylpropane [34]. Non woody lignin also contains mainly hydroxyphenylpropane (5-35%) and low levels of syringylpropane [35][36][37]. Thus, depending on the type of lignin, lignin conversion will result in the production of different proportions of various types of phenols such as phenol, cresol, guaiacol, syringol, etc. [38][39].

Table 1 Lignin monolignols

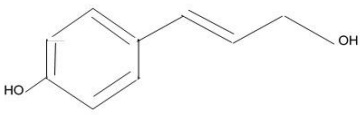
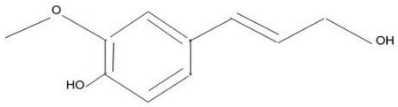
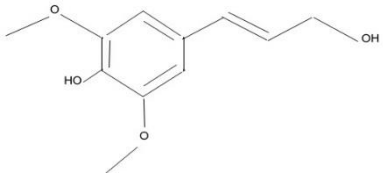
Lignin monomer name	**Chemical structure**
p-Hydroxyphenylpropane unit (H)	
Guaiacylpropane unit (G)	
Syringylpropane unit (S)	

Figure 2 illustrates a simplified lignin structure that shows the various types of chemical bonds between the monomer units [23]. As can be seen from Figure 2, the amorphous structure of lignin is due to the coupling of lignin monomers through polymerisation [40]. In the lignin structure, β-O-4-aryl ether bonds are the major common linkages [36]. Other major linkages are β-1-(1, 2-diarylpropane), 4-O-5-diarylether, β–β-resinol, β-5-phenylcoumaran, and 5–5-biphenyl linkages [21][41]. Due to its complex structure, lignin reactions and processes are investigated by employing model compounds that represent the aforementioned binding units.

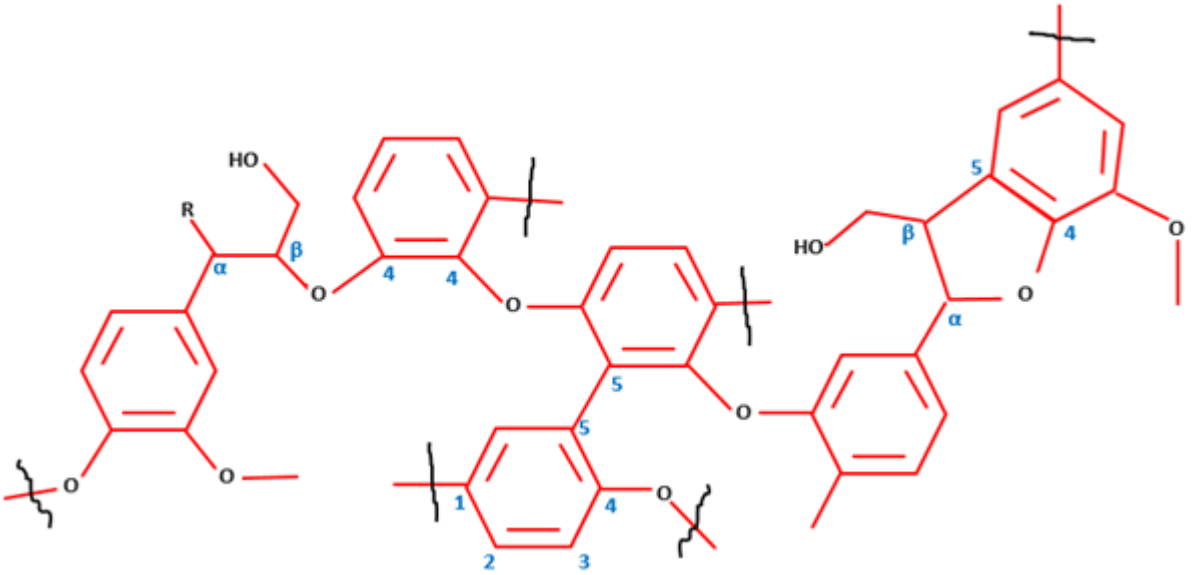


Figure 2 Chemical bonds within the lignin structure (Redrawn from Zakzeski et al [42])

2.3 Lignin sources and isolation methods

Lignocellulose is the main source of lignin, and can be in the form of sugar cane bagasse, wood, straw, grasses, etc. [22][43][44]. Since lignin is part of the lignocellulose structure, it is usually isolated from cellulose and hemicellulose through various means. For example, it can be isolated via pre-treatments such as steam explosion combined with carbohydrate hydrolysis or pulping with sulphite, soda or Kraft methods [21][45][46] .

2.3.1 Steam explosion

It is a pre-treatment process that opens up the lignocellulose structure by employing high pressure saturated steam followed by rapid pressure release [45][47]. High pressure and temperature causes the cleavage of some of the bonds present in the polysaccharides and lignin such as ether bonds [48][49]. This results in catalytic hydrolysis reactions of lignocellulose components by acetic acid that is released by cleavage of the bonds [23][50]. Hemicellulose is hydrolysed into soluble sugars, whilst cellulose and lignin only undergo structural modification [51]. Residual hemicellulose and cellulose that is entrapped onto the lignin structure is removed via enzymatic hydrolysis, which results in lignin with a purity in the range of 86-97% [46][51]. Lignin

produced via the isolation method has the advantage of being sulphur-free thus making it suitable for chemical production [46].

2.3.2 Soda pulping method

Soda pulping is a method that involves use of sodium hydroxide in delignification of non-woody biomass such as sugarcane bagasse and grasses, thus producing cellulose rich pulp [52][21]. Delignification reactions involve radical reactions that results in cleavage of α-O-4 and β-O-4 linkages. This in trurn results in solubilisation and enables sodium ions to form ionic bonds with phenolic hydroxyl and carboxyl groups of lignin via ionic bonds [53][54].

In another study, bagasse lignin, which is of particular importance to this study, produced via this route was found to be composed of β-O-4 alkyl-aryl ether substructures, minor amounts of β-5-phenylcoumarans (6%) and other condensed substructures [35]. It has a H:G:S molar composition of 2:38:60 [33]. The side chain is extensively acylated at the hydroxyphenylpropane unit (42% acylation in bagasse) predominantly with Syringylpropane (i.e. S units) and Guaiacylpropane (i.e. G units) to a minor extent [54][55].

2.3.3 Kraft pulping process

This process involves the use of aqueous sodium sulphide and sodium hydroxide to dissolve lignin and the majority of the hemicellulose present in the lignocellulosic biomass, resulting in a cellulose rich pulp and a black liquor [56]. During the Kraft pulping process, lignin undergoes intensive depolymerisation which results in the formation of carboxylate and phenolate ions [57][58]. Fragmentation of cellulose and hemicelluloses also occurs significantly [14].

Lignin is precipitated from solution via addition of acids such as hydrochloric that leads to a lignin structure that has significant chemical and structural modifications compared to the original lignin structure [34]. Fragmentation of lignin occurs via the cleavage of alpha- and βeta-aryl ether bonds in free phenolic structures, breaking of βeta- aryl bonds in non-phenolic structures, demethylation and condensation. Unlike

in steam explosion and soda pulping processes, lignin produced by Kraft process contains sulphur, which raises some environmental concerns[9][59]. This causes this type of lignin to have limited applications especially when used to produce chemicals.

2.3.4 Sulphite pulping

The sulphite pulping process involves the use of sulphur dioxide and bisulphite of ionic calcium to dissolve lignin and hemicellulose into a liquor called lignosulphonate via sulphonation and hydrolysis [60]. Sulphonation causes the lignin to be more soluble, through cleavage of aryl ether bonds resulting in the production of phenolic hydroxyl groups [61]. Sulphite pulping is a suitable process for both hardwoods (i.e. eucalyptus and poplar) and softwoods such as spruce, hemlock, pine, and fir. Compared to Kraft black liquor, it contains more sulphur due to the presence of lignosulphonate that is formed during hydrolysis of lignin and hemicellulose [60].

2.4 Lignin into phenol conversion technologies

Lignin conversion technologies are namely thermochemical, chemical and biochemical [20] [50][62]. These technologies have the potential for commercial production of desired phenols [63]. As illustrated in Figure 3, each of these technologies produces specific products. Thermochemical processes are namely pyrolysis and fast thermolysis (i.e. gasification) [21][64]. Gasification takes place under conditions of limited oxygen supply (i.e. partial oxidation) and high temperatures around 800-900^{o}C producing a gas mixture which consists of carbon dioxide, hydrogen, carbon monoxide and methane [65][66]. Lignin is converted into a combustible producer gas that can be combusted directly in a boiler to produce heat for steam generation or electricity generation [2][67]. Alternatively, the gas products can be further processed to produce transport fuel through Fischer-Tropsch synthesis [2].

Pyrolysis of lignin is the thermal decomposition of lignin in the absence of oxygen from solid state into solid (char), bio-oil (mainly composed of phenolic compounds) and a non-condensable gaseous mixture [68][69][37]. Biochemical processes are namely enzymatic oxidation and hydrolysis [22][70]. Enzymatic oxidation involves the use of

biological enzymes such as polyphenol oxidative and nutrients so as to convert lignin into phenols (specifically vanillin) [19]. Enzymatic hydrolysis of lignin also involves the use of enzymes, but it differs in that it uses hydrolytic enzymes called hydrolases that use water to depolymerise lignin into phenols [71]. Chemical processes comprise mainly of hydrolysis and hydrogenation. Chemical hydrolysis involves the use of inorganic chemicals to depolymerize lignin by breaking the intermolecular bonds, thus turning it into phenols [72]. Hydrogenation of lignin involves use of hydrogen together with metallic catalysts in order to convert lignin into phenols [27][70].

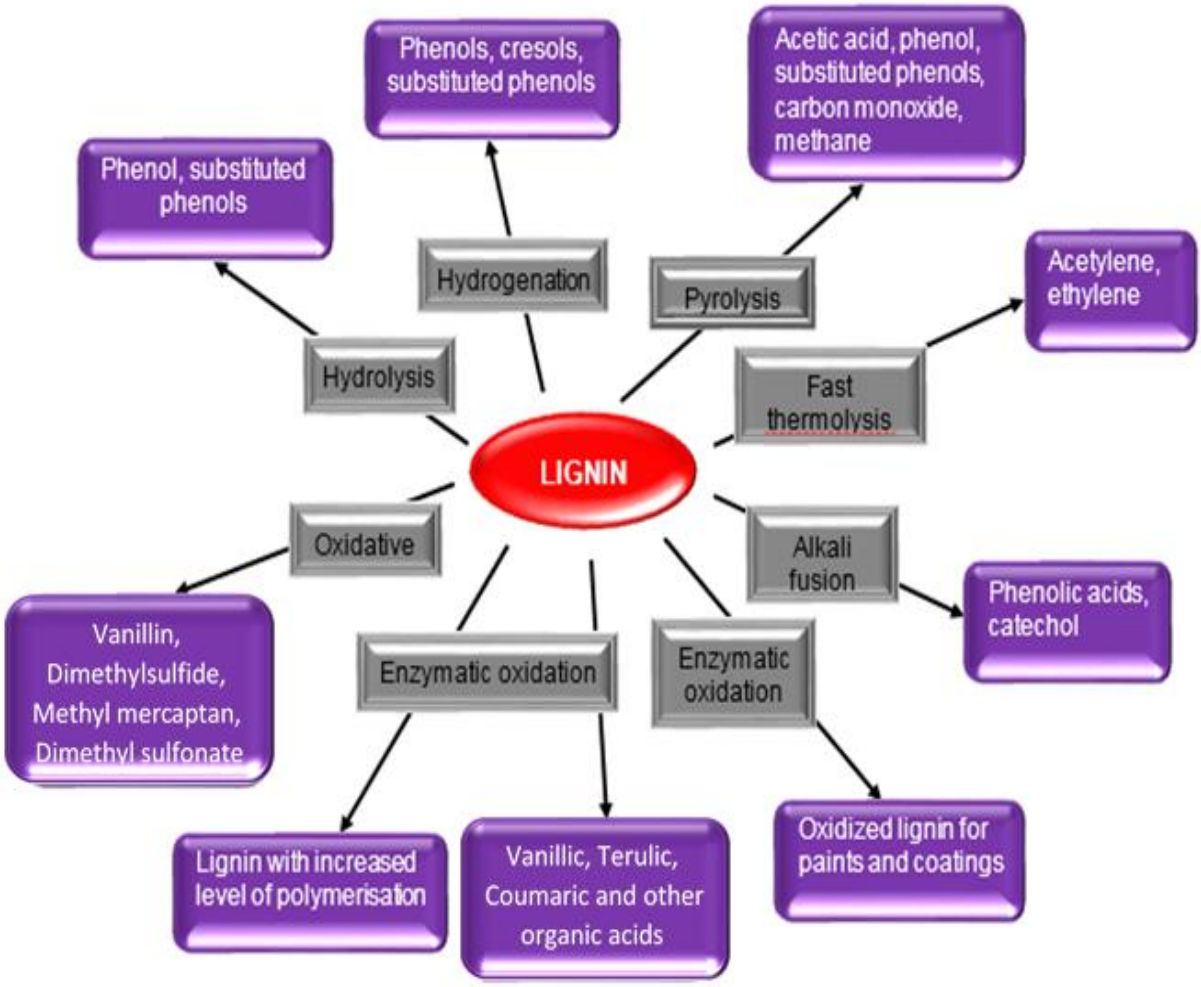


Figure 3 Lignin conversion technologies (Modified from Holladay et al [25])

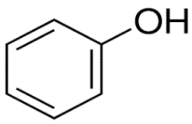
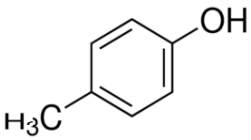
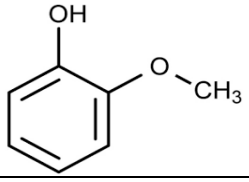
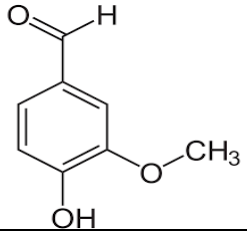
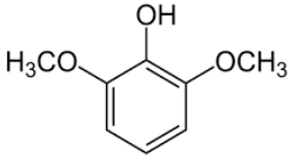
All the approaches shown Figure 3 have borne substantial understanding into the lignin based value added chemical products whereby the main challenge is low yield and non-selectivity of products [44][73]. Catalysts have been employed in several

technologies such as chemical hydrolysis in the effort of increasing yields of phenolic compounds but this has also produced low total yields of phenolic compounds (i.e. 0.5 – 4.9 wt.% lignin) [74][75]. An example is the production of phenolic chemical products via chemical depolymerisation of lignin with both cheaper (metal hydroxides and carbonate combined with solvents) and costly ionic catalysts liquids and transition metals supported on carbon [71][76]. Phenolic compounds yields obtained by liquefaction remain low (i.e. 0.9 – 1.5 wt.% lignin) despite the use of catalysts, thus the yield requires improvement [77][72].

Currently two processes show high potential to economically convert lignin into phenolic compounds, i.e. enzymatic oxidation and pyrolysis. Enzymatic oxidation of lignin has the main drawback of long production times [77]. Also the use of enzymes, typically produced by appropriate microbes, makes the process operationally complex, also in terms of the separation of phenolic compounds from the de-polymerised lignin. Unlike enzymatic oxidation, pyrolysis process is operationally simpler, instant conversion of lignin into phenolic compounds, can easily depolymerise any type of lignin and the concentrated phenolic product mixtures are more suitable to fractionation into individual products/fractions [15][16]. Thus based on these observations, pyrolysis was found to be the process that could potentially economically convert lignin into phenolic compounds.

Phenols are aromatic chemical compounds that contain phenyl and hydroxyl groups [5]. Depending on the functional group that is bonded to the phenyl group, phenols will have specific properties and names as demonstrated in Table 2.

Table 2 Types of phenols and their applications [75]

Phenolic	Chemical Structure	Chemical Properties	Uses	Market value (US$ per tonne)
Phenol		Soluble in water, Sweet and tarry odour, Boiling point of 181.7 °C, Melting point of 40.5 °C	Making resin, pharmaceutical products, solvents	1100 – 1500
P-Cresol		Soluble in water, Sweet and coal tar odour, Boiling point of 191.0 °C, Melting point of 29.8 °C	Pharmaceutical products, fragrance products, solvents	6000 - 8000
Guaiacol		Soluble in water, Sweet and tarry odour, Boiling point of 205 °C, Melting point of 28°C	Precursor to various products such as fragrance, flavouring products,	4800 - 6000
Vanillin		Soluble in water, Sweet odour, Boiling point of 285°C, Melting point of 83°C	Making food products, fragrance,	10 000 – 12 000
Syringol		Soluble in water, Sweet and tarry odour, Boiling point of 261°C, Melting point of 50°C	For preparing smoked food products, resins	4800 - 6000

As can be seen from Table 2, the functional groups that are bonded to the benzene ring influence the chemical property of that specific phenol. Thus they differ in terms of areas of application [38]. These phenols are mainly used in the automotive, wood and electronic industry. In the automotive Industry, phenols are used in the moulding of automotive parts [13]. Demand for phenol in this area is expected to growth for the next 10 years due to innovations in these industries[13]. The wood industry mainly uses phenols to make adhesives and varnishes. But the need to recycle wood in order to conserve trees, which is now one of the major factors driving up demand for these phenolic end products in this industry where they are used to fabricate planks from recycled wood [16]. In the electronic industry, phenolic compounds are used to mould

components that are used to make DVDs, CDs, phone covers, storage devices, computers etc..

Currently the majority of the phenols are produced from fossil based resources via three main processes namely Cumene, Raschig and Sulphonation [1]. In the Cumene Peroxidation process, phenol is produced from a cumene emulsion that involves reacting benzene with propylene at 160-260°C in the presence of phosphoric acid catalyst [78]. The Raschig process is the catalytic conversion of benzene into chlorobenzene at 36°C in presence of a copper iron catalyst and hydrochloric acid [79]. Thereafter chlorobenzene is hydrolysed by steam into phenols over a silica catalyst. In the Sulphonation process benzene is first converted into benzene sulphonic acid by reacting it with concentrated sulphuric acid at 150-170°C and thereafter the benzene sulphonic acid mixture is neutralised by sodium sulphite into a sodium phenate solution [1][80]. When this salt is fused with sodium hydroxide, a crude phenol solution is formed.

2.4.1 Lignin Pyrolysis

Pyrolysis is the thermal conversion of lignin in an oxygen deficient environment into bio-oil, char and gases as the main products [81]. Pyrolysis reactions occur in two stages namely primary and secondary reactions [75][82]. Primary reactions involve the degradation of the lignin into volatile products, whilst secondary reactions involve the thermal cracking and the recombination reactions of the volatiles produced during the primary pyrolysis reactions [82].

When lignin condensable volatiles separate from non-condensable gases they produce bio-oil, which is a mixture of several phenol-derived monomers (complete depolymerisation) and oligomers, mostly composed of 2-5 monomer units [69]. The complexity, high molecular mass and poor volatility of lignin derived oligomers limit their detection and characterisation by analysis machines such as the GC-MS [24][34]. Ma et al [59] reported that approximately 40 wt.% of lignin bio-oil could not be detected by GC and therefore, required other analytical methods such as Fourier

Transform Infra-Red (FTIR), Gel Permeation Chromatography (GPC). Currently the complexity surrounding the pyrolysis of lignin is limiting its commercial viability, thus improvement in the depolymerisation of lignin to obtain phenols requires a critical approach [16][64].

The most common phenols identified in lignin bio-oils are guaiacol, alkylguaiacol, syringol, syringaldehyde, vanillin, vanillic acid, catechol, cresol, eugenol, phenol, alkyl phenol, etc. [6][24]. The yields of these compounds are highly variable due to their dependence on the operating parameters such as temperature, heating rate, gas residence time and feed composition [21]. Through understanding how these operating parameters influence the lignin pyrolysis process, side reactions can be predicted, thus helping controlling the formation of the products of interest (i.e. phenols) [83]. Yields of the mono-phenols are not significant in non-catalytic pyrolysis of lignin, thus catalytic options have been explored to improve both selectivity and yields [59]. There are several reports on lignin pyrolysis experimental studies, using different analytical techniques such as TGA coupled with on-line analysis of evolved volatiles using FTIR or MS, and pyrolysis at bed scale using GC-MS to analyse the produced bio-oil composition [24][84][85][86]. While TGA studies are useful to investigate pyrolysis mechanisms and the influence of temperature on the stability of the various chemical functions, studies at bed scale give more precise information about the yield trend of the components [58].

Pyrolysis processes that are used for lignin de-polymerization fall under three categories namely fast, intermediate and slow pyrolysis;

1. *Fast pyrolysis* - occurs at temperature in the range of 300 - 550°C, with a volatiles residence time of less than 2 seconds and heating rate of 1000 -1500^{o}C per minute [87][88][89]. Product distribution from fast pyrolysis of lignin is characterized as 25 – 48% char, 45 – 56% liquid and a 5 – 16% gases based on the reactor and type of lignin used [56][90][91][92]. Lignin pyrolysis produces more char than pyrolysis

of lignocellulose mainly due to the presence in lignin of thermally stable benzene ring that requires more energy for cleavage.

Figure 4 illustrates an existing fast pyrolysis unit at the Department of Process Engineering at Stellenbosch University that was drawn for the purpose of this study. As seen from Figure 4, lignin is first force-fed into the pyrolysis reactor that contains hot fluidised media (sand) where it is heated up quickly and thus undergoes decomposition into char, gases and phenolic vapours. Fluidisation enables lignin particles to remain in the reactor until fully pyrolysed into char. When lignin particles are fully pyrolysed, then they are sufficiently light to enable entrainment in the gas stream, thus exiting the reactor as char [93][94]. Thus, fluidisation is also for control of solids residence times, and separation of fully-pyrolysed lignin from the incompletely-pyrolysed lignin.

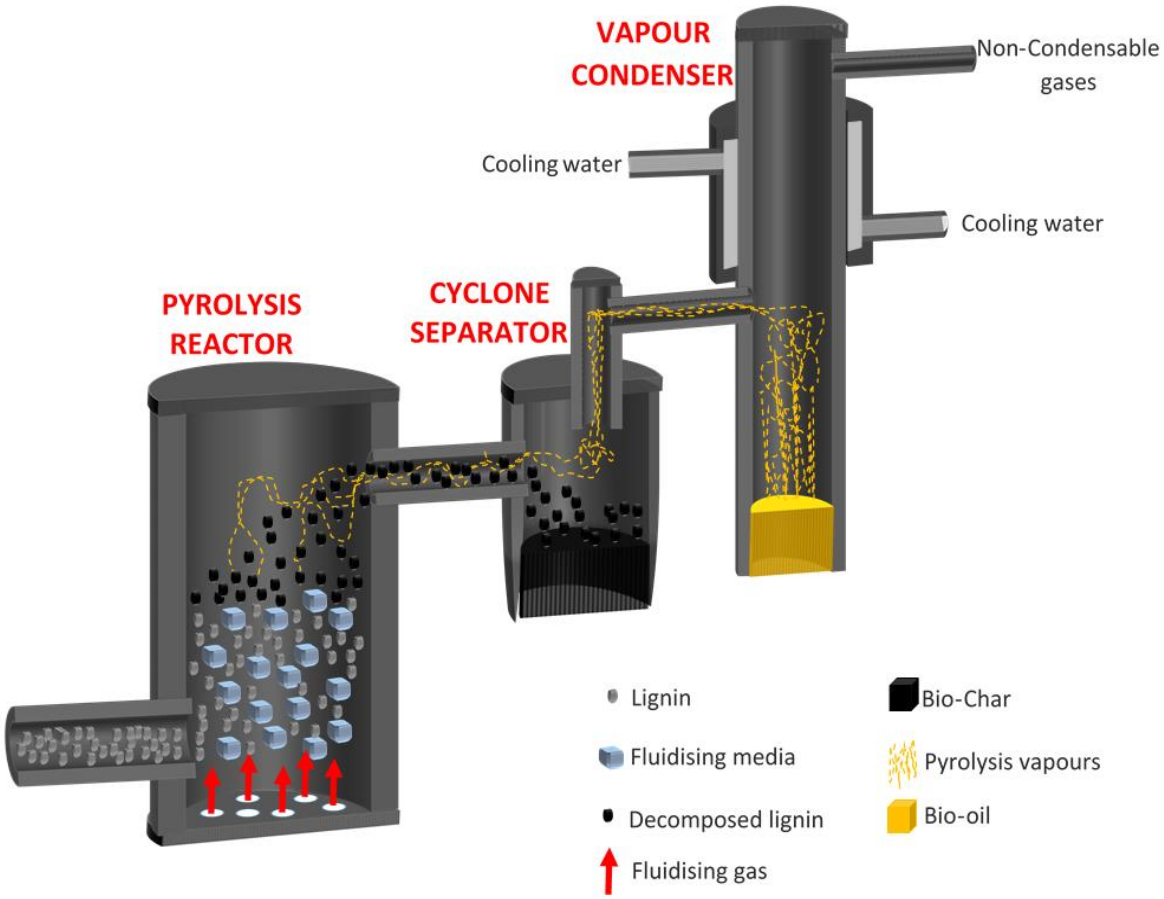


Figure 4 Fast pyrolysis unit

When the char and vapours exit the reactor, char by virtue of its weight is separated and the centrifugal force in the cyclone, it descends to the bottom of the cyclone separator whilst the vapours exits via the top of the cyclone separator and proceed to the condenser. In the condenser, the phenolic vapours condense into bio-oil, whilst the non-condensable gases such as carbon monoxide exit the condenser into the exhaust system.

2. *Intermediate pyrolysis* – It offers an alternative to fast pyrolysis for better control of products by controlling the residence time, operating pressure and heating rate. With regards to phenolic rich bio-oil, it produces lower yields of bi-oil compared to fast pyrolysis. Intermediate pyrolysis occurs at average temperatures of 350 - 450°C at a heating rate in the range 11 - 120°C per minute [46][81][95]. The volatiles usually have a residence time of less than 4 seconds, which can be attained by controlling the pressure in the reactor [21][89][95]. Depending on the types of lignin and reactor applied, the products of intermediate pyrolysis of lignin are characterised as 35 - 60% liquid, 15 - 25% gases and 20 - 39% char [96][97][98].

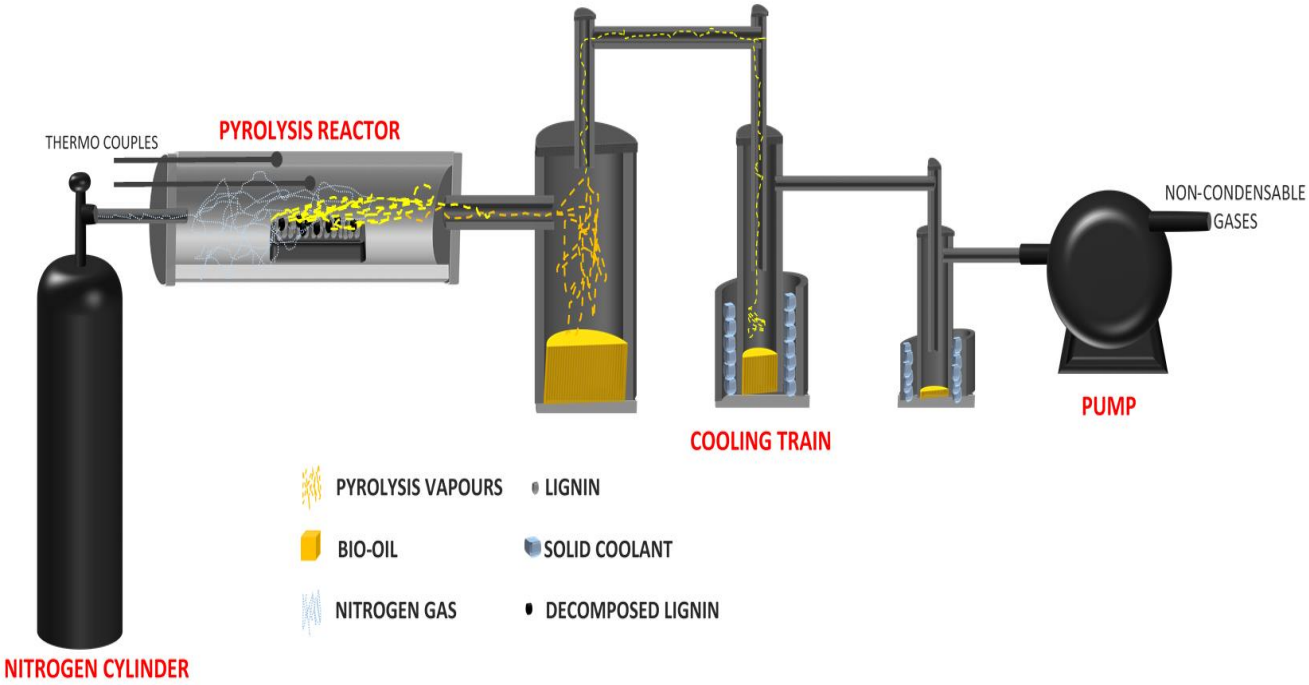


Figure 5 Slow/Vacuum pyrolysis unit

Figure 5 illustrates an intermediate pyrolysis unit at the Process Engineering Department of Stellenbosch University. The equipment consists of a quartz tube

reactor that houses the sample, which is heated by insulated automated elements. Nitrogen gas is used to purge the oxygen out of the pyrolysis equipment so as to prevent oxidation of volatiles, and thereafter the vacuum pump is applied to maintain gas flow out of the reactor. When the sample is heated, the lignin sample decomposes under a negative pressure from the vacuum pump. The condensable volatiles are then collected from five condensation train held at different temperatures connected to the heated chamber.

3. *Slow pyrolysis* – It occurs at average temperature of 400 - 500°C [43][99][100]. Slow pyrolysis is associated with low heating rates of 5 – 50°C per minute and long residence times [81]. Depending on the type of lignin and reactor applied, products of slow pyrolysis of lignin are characterized as 30 – 45% liquid, 25 - 43% gas and 30 - 45% char [81][87][101]. Slow pyrolysis has the advantage of ease of operation since the design of the equipment is not complex. Its main disadvantage is that compared to fast and intermediate, it produces low yields of the phenolic rich bio-oil which is not favourable when attempting to economically produce phenols from lignin. The low bio-oil yields are due to the long residence time that result in secondary reactions of lignin vapours. Secondary reactions involveconversion of lignin volatiles into secondary char, aromatics, hydrocarbons, carbon dioxide and carbon monoxide. When the pump in Figure 5 is removed, the equipment becomes a slow pyrolysis unit. During pyrolysis, nitrogen is first used to purge the reactor and thereafter as carrier gas for the volatiles and non-condensable gases, whilst the cooling train serves the same purpose mentioned above of condensing volatiles.

2.4.1.1 Parameters influencing pyrolysis of lignin

Pyrolysis is influenced by a variety of parameters namely reactor temperature, heating rate, and particle size. Since these parameters are dependent on each other, they will have an effect on the product spectra of desired components[12][21].

2.3.1.1.1Temperature

Lignin decomposes at higher temperature ranges (200-600^{o}C) than cellulose and hemicellulose due to thermal stability of the benzene ring that enables chemical bonds present in the lignin structure to resist cleavage [56][86]. Since these functional groups behave differently during heat treatment, it has been proposed that step-wise pyrolysis could be a means to produce products with high purity, thus simplifying separations [33][76][102]. In order to obtain specific yields of desired components, the heating source is used to control the pyrolysis temperature within specified settings [50][56]. Also depending on the type of pyrolysis method, the yields of desired components will vary with temperature hence temperature is one of main variable affecting pyrolysis [83][103].

The thermal treatment of lignin begins with the elimination of moisture below 200^{o}C and thereafter follows the primary stage of lignin pyrolysis depolymerisation, which covers a wide temperature range of 200-450^{o}C [21][104][41]. Most primary volatiles are released within this temperature range, due to the unstable nature of alkyl chains, some beta-ether linkages between the lignin building block units, and aromatic ring substituents such as the methoxy functional groups (CH_3O-)[50][104][61]. Non-condensable gases such as methane and methanol are formed from the fragmentation of methoxy groups, whilst condensable vapours of chemical products such as formic acid and formaldehyde are formed from the fragmentation of the alkyl side chain [32][69]. The majority of the phenolic compounds such as syringol, phenol, guaiacol and their derivatives are evolved at this stage[25].

The last stage of thermal degradation of lignin occurs at temperatures above 450^{o}C, which is related to an increase in the production of non-condensable gases due to secondary reactions [100][105]. For example, Collard et al [22] showed that at high temperature of around 600^{o}C, the scission of the aromatic ring substituents can result in the formation of the non-condensable gases (CH_4, CO and H_2).

In lignin pyrolysis, volatiles are mainly composed of phenolic compounds at temperatures in the range 200 – 550°C [100]. But above 550°C, the phenolic compounds are cracked into aromatic hydrocarbons and gases [85][61]. Thus an increase in temperature generally influences the properties of the liquid fraction, where the oil is largely phenolic at low temperatures and shifts more to production of high yields of benzenes at higher temperatures [12][58].

2.4.1.1.2 Volatiles residence time

The residence time of the volatiles is influenced by the type of reactor used for pyrolysis and also the flow rate of the carrier gas or the eventual vacuum pressure[30]. It was reported by Jegers et al [100] that the yields of phenolic compounds are higher in fast pyrolysis, due to the low residence time that prevents further degradation of phenolic compounds into benzene and other cyclic hydrocarbons. It has also been reported by Wild et al [15][106] that longer residence times can also result in re-polymerisation of the lignin monomer derived compounds into secondary char, thus further reducing the yields of the phenolic compounds. Also in lignin pyrolysis, phenol oligomers are formed (directly and through secondary reactions), which in turn results in low yields of simple phenolic compounds such as phenol, ethyl phenol, methyl phenol, etc. [69][56].

2.4.1.1.3 Heating rate

Heating rate is one of the key variable of pyrolysis that is used to control the rate of reaction [107]. The heating rate is determined using equation (1).

$$T = (HR).t + T_0 \qquad \textit{Equation 1}$$

Where;

T – Maximum temperature (°C)

HR – heating rate (°C/min)

t – Total heating time (minutes)

T_0 – Initial Temperature (°C)

An increase in heating rate generally increases the degradation rate, and thus high heating rates (such as the case in fast pyrolysis) imply high reaction rates, as compared to slow pyrolysis [21][108]. Slow pyrolysis of lignin is conducted at low heating rates (i.e. 5 – 50^{o}C per minute), where char is the main product of interest [87][109][110]. Low heating rate favours the progressive breakdown of most unstable functional groups and rearrangement reactions during lignin pyrolysis, which results in bio-oil containing desired phenolic compounds in low yields.

Fast pyrolysis is conducted at higher heating rates (i.e. 1000 -1500^{o}C per minute) where bio-oil is the major product [12][88][86]. At a high heating rate, many of the oxygenated functions within phenol derivatives and hydrocarbons chains are simultaneously broken, with the exception of the very stable hydroxyl substituent of the phenols benzene ring [21]. Although secondary reactions can occur under high heating rates, yields of phenolic compounds are high due to short vapour residence times that limit further decomposition of phenolic compounds [111][112].

2.4.1.1.4 Particle Size

During pyrolysis, temperature gradients develop within particles, which in turn affects the kinetics of a pyrolysis process, thus influencing on the rate of heat transfer within the particle and the yields of desired components [113]. Temperature gradients tend to be more pronounced in large particles as compared to small particles, thus leading to higher yields of char, as the majority of the volatiles and gases takes longer to be evolved [114][101]. Thus if low residence time is desired, small particle sizes are preferred.

A dimensionless quantity that relates particles to other pyrolysis process parameters is the Biot number as given in equation (2);

$$Bi = \frac{h.Dp}{k} \qquad \textit{Equation 2}$$

Where;

Bi – Biot number

h – Heat transfer coefficient ($W.m^{-2}.K$)

D_p – Particle diameter (m)

k – Thermal conductivity ($W.m^{-1}.K$)

So as can be seen from equation above, if the D_P is small, the Biot number is low.

2.4.1.1.5 Reactor configuration and Scale

Different pyrolysis reactor configurations can be used to convert lignin into various chemical products [30][115][116]. The reactor configuration can be at analytical level (i.e. TGA milligram scale), at bench scale level or at pilot level. For example at analytical level, there is the wide use of reactor configurations such as pyro-probe and platinum coil reactors that are coupled to gas chromatography mass spectrometer [76][117]. Bench scale configurations can be in the form of centrifuge and glass tubular reactors with condensation trains and also small fluidised bed reactor [92][118].

In literature, reported lignin pyrolysis studies used either milligram or gram/kilogram-scales of lignin feed and were operated under different conditions using various lignin types [69][117].

2.4.1.1.6 Catalysts

During lignin pyrolysis, formation of oligomers results in low yields (i.e. less than 1 wt.% of lignin) of phenolic compounds such as phenol, o-cresol, etc. [76][88][119]. Figure 6 illustrates an example of catalytic pathways of lignin pyrolysis. Figure 6 depicts the series of reactions that occur during conversion of the oligomers into phenol monomers over HZSM-5 catalyst [95][111]. It can be seen that lignin first decomposes into simple monomeric phenols and oligomers. The oligomers are then depolymerised into simple phenols and aromatics over the HZSM-5 catalyst, which thereafter becomes deactivated. The catalysts lower the activation energy needed for the cleavage of bonds linking lignin monomers, thus increasing the number of bonds broken at any pyrolysis temperature [84][36]. When the active sites of the catalyst becomes blocked by char and fine lignin ash, the catalyst becomes deactivated [120].

Char has to be burnt off the active sites of the catalyst, to regenerate the catalyst [121][122].

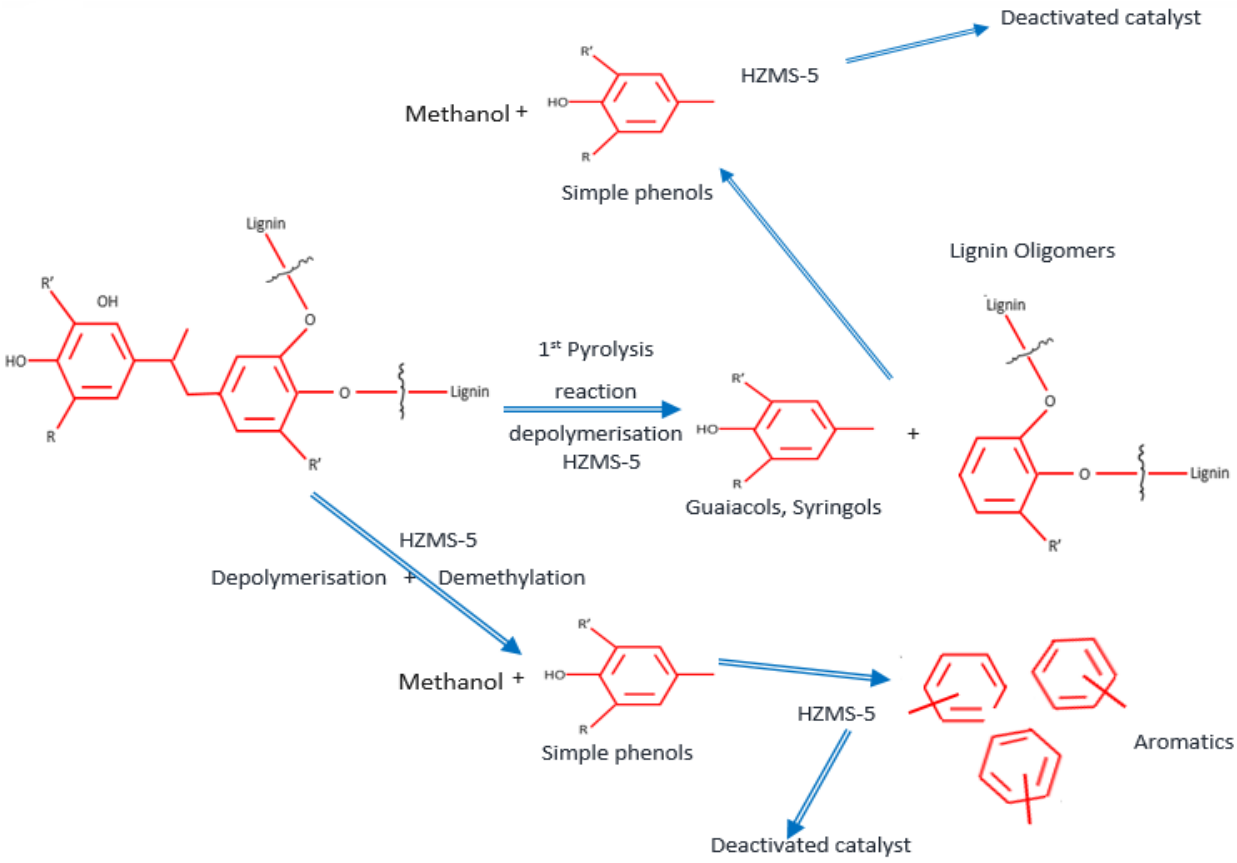


Figure 6 Pathways for catalytic depolymerisation of lignin over HZSM Zeolite catalyst (Redrawn from Dickerson et al [111])

Non-catalytic pyrolysis of lignin produces a wide distribution of multi-functional phenolic compounds in lower concentrations than when catalysts are applied. Since optimisation of all the parameters is not enough to produce significant yields of phenols, pyrolysis of lignin over different catalysts appears as an option to produce high yields of valuable chemicals [58][123]. The performance of a particular catalyst is affected by numerous conditions such as access to active sites of the catalyst by reacting species, thermal stability of the catalyst, etc. To enable more contact between reacting species and the catalyst active sites, the catalyst can be either directly mixed or impregnated with the lignin. Studies on catalytic pyrolysis of biomass by authors such as Collard et al [22], and De Wild et al [6] have shown that both

methods have an impact on the yields of phenolic compounds as they promote better contact between the catalyst and lignin.

Catalysts have major influences on the yields of oil, gas and char produced during pyrolysis of lignin [56][124]. For example, Bridgwater et al [125] and Fierro et al [126] found that during pyrolysis of biomass impregnated with NaCl, orthophosphoric acid and $ZnCl_2$ as catalysts, char formation was promoted compared to the yield of the oil produced. Although zeolite catalysts are known to be expensive compared to other catalysts used in studies of lignin pyrolysis, the abundance of availability of the literature of catalytic pyrolysis of lignin using zeolite made this catalyst relevant to this study [88][120][127].

Table 3 Typical Chemical Products obtained from Catalytic Pyrolysis of Lignin

Lignin Name	Catalyst	Pyrolysis Reactor	Temperature (°C)	Yield (wt. %)	Product	Reference
Alkaline lignin	MoO_3, NiO, Fe_2O_3, MnO_3, CuO	Pyroprobe pyrolyzer	650	<15 (peak area)[a]	Vanillin	[20]
Alkaline lignin	Ni-HZSM-5, Cu-HZSM-5, Fe-HZSM-5, Mo-HZSM-5, Co-HZSM-5	Pyroprobe pyrolyzer	500-650	<15 (peak area)[a]	BTX, phenols	[128]
Kraft lignin	TiO_2	Pyroprobe pyrolyzer	550-600	>21	Phenols	[76]
Alkaline lignin	NaOH, KOH, Na_2CO_3, K_2CO_3	Quartz fixed bed reactor	450	>30	Phenols	[56]
Wheat straw-derived organosolv lignin	Nil	1kg/h bubbling fluidised bed reactor	500	7.0-11.0	Phenols	[106]
Alkaline lignin	Activated carbon	Microwave-assisted pyolyzer	350-591	45 (peak area)[a]	Phenols	[69]

[a] in some studies, only peak area of the GC-MS analysis of the oil is reported

Table 3 shows that catalysts have specific selectivity for particular chemical products obtained from lignin pyrolysis, and that the yields of the phenolic compounds vary based on the type of catalyst and lignin used. Peak area gives information about product selectivity but cannot be considered as an actual mass yield. It can be seen

from Table 3 that alkaline lignin produced the highest yields of phenolic compounds (i.e. yield >30 wt.% lignin) whilst organosolv lignin had the lowest phenolic yields of 7 – 11 wt.% lignin. It is worth noting that the organosolv was a non-catalytic pyrolysis process whilst for the alkaline lignin it was a catalytic pyrolysis process.

As can be seen in Table 3, alkaline catalysts have a potential to increase yields of monomeric phenols and since they are readily available and cheap, they have a potential to lead to an economic conversion of lignin into phenolic compounds [63]. Several studies have shown that alkaline catalysts are promising catalysts in lignin depolymerisation into phenolic compounds [30][72]. Non-catalytic pyrolysis of lignin produced 6-9.5 % of phenols based on peak area, while the various catalysts produced phenols in the range of 13.0-32.6% based on peak area [20][85]. NiO catalyst produced the highest phenols with a peak area of 32.6% [31].

A number of studies are focused on degradation of lignin to a mixture of chemical products, while reports on the selective catalytic depolymerisation of lignin to phenols, for high value applications, are limited. Thus screening of catalysts for use in the development of the Aspen Plus models was also based on data availability.

2.4.1.1.7 Feedstock

Lignin source is another major parameter that affects pyrolysis is the composition and type of feedstock used for pyrolysis [116][129]. In the case of lignin pyrolysis, the lignin is characterised using the various methods namely Proximate and Ultimate Analysis, Nuclear Magnetic Resonance (NMR) spectroscopy and TGA - GC/MS spectroscopy. These methods enable functional groups of lignin to be identified, composition of lignin, and its structure [70][126]. The major variable of the feedstock is wide range of lignin properties, based on raw materials and isolation methods. Since lignin samples are different, each lignin sample will have different impacts on the yields and product spectra produced during pyrolysis.

2.4.1.1.7 Other parameters

Pressure also has an influence on the product distribution in pyrolysis reactions. Vacuum pressures result in shorter volatiles residence times, thus limiting the occurrence of secondary reactions [46][102]. Vacuum pressure also enhances diffusion within the particle, which consequently reduces residence time of volatiles produced within the particle. It also reduces the required pyrolysis temperature and also modifies the quality of char product (porosity), due to minimisation of the volatile carbonisation secondary reactions that deposit on the char surface[100].

2.5 Fractionation of phenols from pyrolysis liquids

The viscous dark liquid product (known *as bio-oil* or pyrolysis oil) that is formed during lignin pyrolysis contains condensable volatiles such as phenols, esters, water aldehydes and organic acids [69][129]. Of all the composite constituencies present in bio-oil, phenols have a relatively higher market value (i.e. US$1500 – 10 000 per tonne) [13][16]. Biorefinery processes facilitate the extraction of valuable products like biofuels and commodity chemicals through fractionation[51][15]. In the biorefinery, fractionation of selected key chemicals or fractions is achieved via fractional condensation, liquid-liquid extraction, chromatography and fractional distillation. Table 4 shows reported lignin recovery technologies in literature that have been used to investigate recovery of high yields of phenolic compound from bio-oil. Fractional condensation involves condensing the hot vapours of lignin pyrolysis into fractions via several condensers maintained at different temperatures [19][58]. Since vapours from lignin pyrolysis contain 25 – 30% water, fractional condensation can reduce the moisture content of lignin based bio-oil, thus reducing downstream costs. Studies in fractional condensation of pyrolysis vapours by Tumbalam et al [133] and Westerhof et al [134] showed that fractional condensation can reduce moisture content of bio-oil to less than 1%. Thus this process is highly favourable in terms of application in phenol recovery.

Table 4 Lignin based phenol production process analysis

Feedstock	Catalyst	Type of reactor	Pyrolysis Temperature (°C)	Phenols recovery method	Phenolic compound yield (wt.% bio-oil)	Reference
Sugarcane bagasse	Non catalytic	fluidised bed reactor	499	supercritical fluid extraction (*At 300 bar, 59.8° C, 1.2 kg/hr*)	30	[130]
Birch wood	Non catalytic	fluidised bed reactor	500	Steam Distillation (*steam: oil ratio of 27, 10kPa, 200° C)*	21.3	[39]
Organosolv lignin and soda lignin	Ru/C, Ru/Al_2O_3 Ru/TiO_3	bubbling fluidized bed reactor	400 – 500	CO_2 supercritical fluid extraction	10	[131]
Corn Stalk lignin	Non catalytic	Fluidised bed reactor	477 – 480	CO_2 supercritical extraction (*At 300 bar, 35° C,*)	31 - 41.	[132]

Once the bio-oil fractions from condensation have been obtained then liquid-liquid extraction using a suitable solvent, can be used to extract phenolic compounds from these bio-oil. Although liquid-liquid extraction at cryogenic conditions produced relatively satisfactory yields of phenolic compounds, the operations requires specialised equipment for operation and is also prone to high operating costs. Since lignin bio-oil is highly viscous (greater than 900 Pa.s), liquid-liquid extraction of phenols using liquid solvents requires temperatures above 100°C, where the viscous bio-oil can easily flow and mix with the solvent [11][135]. Phenolic compounds in bio-oil have a boiling point range of 180 – 240^{o}C, they are thermally stable at temperatures above 100^{o}C [136][137]. In the case of fractionation of phenols, fractionation will involve using solvents that can dissolve specific phenols and also recovery of all the solvents thus making the process expensive[138].

Chromatography involves separation of components by passing them under the influence of a mobile phase through an adsorption column [86]. This process is mainly used for analytical purposes although chromatography for large scale industrial application has recently been introduced for commercial application. Although the

process is able to fractionate the phenols, it has the drawback of being expensive and more suitable for small scale application.

Fractional distillation involves separation of a liquid mixture into fractions based on the differing boiling points of the components [139][140]. Since phenolic compounds in bio-oil have a boiling point range of 180 – 240^{o}C, they are stable enough to be fractionated at temperatures in the range of 200 – 250^{o}C where the phenolic mixture reaches boiling point that releases phenolic vapours [139][39][137]. Although it is an energy intensive process, it fractionates the phenols easier compared to the three above mentioned processes. Thus fractional distillation and fractional condensation were chosen as the two methods with a higher potential to produce phenolic fractions economically.

2.5.1 Fractional condensation of phenolic vapours

Studies on fractional condensation of lignin pyrolysis vapours are well documented. For example in the works of Gooty et al [133], an optimum condensation temperature of 80^{O}C was used to obtain a phenolic mixture with a moisture content of less than 1 wt.% [74]. Since the boiling point of water is 100°C, at this temperature a major percentage of the water will escape with the non-condensable gases, whilst the phenols that have a boiling range 180 - 230°C easily condense out of the vapours [75]. As the water vaporises out of the phenolic solution, it entraps some of the phenols. The small portions of the phenolic compounds lost to the gas stream can be burnt in a combustor since the phenolic compounds are toxic by nature.

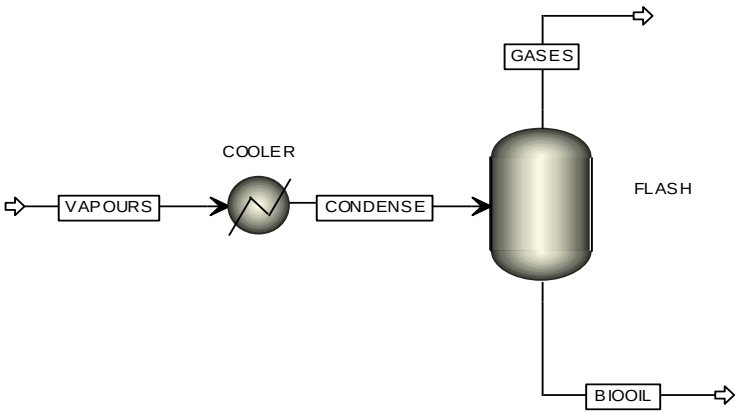


Figure 7 Fractional condensation unit[141]

2.5.2 Fractional distillation of concentrated phenolic solution

Research studies on fractionation of bio-oil into value added chemicals have not been reported in detail, but instead most literature data is on upgrading of bio-oil into transportation fuel. A study by Ne et al [95] combined steam distillation with reduced pressure distillation in order to fractionate lignocellulose based bio-oil. A syringol phenolic fraction was produced, which was further purified to 92.3% by reducing the water content using liquid-liquid extraction [95]. Lignocellulose based bio-oil contained organic acids and other low boiling point organic compounds that decompose at temperatures above 200^{o}C (i.e. the distillation temperature of phenolic mixture) thus making it thermally sensitive. Hence fractionation of lignocellulose based bio-oil is not feasible by conventional distillation methods [139][140]. But unlike lignocellulose bio-oil, lignin based bio-oil contains mainly phenols which are thermally stable thus conventional distillation is appropriate for fractionation of phenolic mixture [39][139].

Fractionation of lignocellulose based bio-oil into value added chemicals needs a strategic market approach, to produce fractions that have attractive market prices, to maximise financial value [16]. Although data on fractionation of lignin pyrolysis biooil is not reported, fraction of lignocellulose bio-oil has been reported in literature. For example, Mullen et al [139] fractionated lignocellulose based bio-oil using molecular

distillation into a product fractions composed of a light fraction, middle fraction and heavy fraction. The light fraction was rich in carboxylic acids, middle fraction composed of esters and aldehydes and a heavy fraction composed mainly of pyrolytic lignin and sugar oligomers.

However lignin based bio-oil contains mainly high boiling point phenolic compounds (i.e. 180 – 270°C) thus conventional distillation could be used to fractionate the phenolic mixture [73][139]. Since data on fractionation of lignin based bio-oil is not available in literature, it was imperative to study distillation of other forms of liquid oils that contain similar composition and types of phenolic compounds. One example is the liquid oil called coal tar that is produced during the distillation of coal [137]. Fractional distillation of coal tar produces light oil (up to 210°C), carbolic oil (up to 240°C), creosote oil (up to 270°) and anthracene oil (up to 300°C)[65][139][137]. Since coal tar contains similar phenolic compounds (i.e. cresol, phenol, guaiacol, etc.) as lignin based bio-oil, fractionation of lignin bio-oil could be based on the temperature profiles of coal tar distillations and the number of produced fractions.

A fractionation column is generally divided into three parts, namely the rectifying section, feed section and stripping section. Due to the vapour-liquid equilibrium in the rectifying and stripping sections, the crude mixture separates into light components and heavy components based on differences in boiling temperatures [39][139]. Parameters that are used to indicate the ease of separation between compounds are relative volatility and difference in boiling points of the components. For example the relative volatility of component *i* to component j as shown in equation (3):

$$\propto = \frac{Xi/Yi}{Yj/Xj} \qquad \textit{Equation 3}$$

X and Y are concentrations in the liquid and vapour phase respectively.

Hence the larger the difference in volatility, the easier separation.

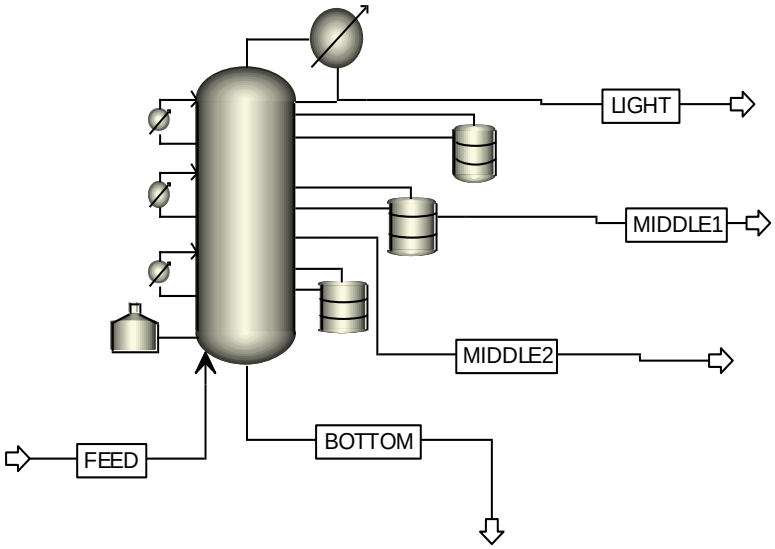


Figure 8 Fractional distillation unit[141]

Since bio-oil is a multi-component mixture that is composed of at least 30 phenols, fractionation of the phenols needs to be based on the specification of the non-key components and key components [142]. For this particular model, the non-key components are phenols with low yields whilst the key components are the phenols with the highest yields. Prediction of the distribution of the non-key components is performed using the Fenske equation where the relative volatility of the non-key components is determined relative to that of phenol. Literature study has shown that the fractionation of the concentrated phenolic solution into individual phenols is not feasible, since phenols form azeotropes in solution with each other [95][136]. Thus it is more feasible to fractionate them into phenolic fractions that are available on the market as shown in Table 5. This principle is also applied in distillation of coal tar, where the residue exits as creosote that is sold to resin producers. Selection of the phenolic fractions is based on the phenolic compound with the highest yield in bio-oil. The phenol market fractions with these phenolic compounds as the dominant fraction are shown in Table 5.

Table 5 Targeted phenols for production [13][143][144][145][146][147]

Phenolic fraction name	Fraction composition	Application	True Boiling point cuts (°C) *
Cresol	60% p-Cresol, 30% Phenol, 10 % o-Cresol	Manufacturing of resin, making medicine	180 – 200
Syringaldehyde	40% Syringaldehyde, 25 % Syringol, 30% Ethyl phenol, Other phenols	Additive in foods such as whisky and smoked flavoured food additives	210 – 240
Syringol	60% Syringol, 40% Ethyl phenol, 10% Other phenols	Manufacture of smoked flavoured food additives	220 -240
Guaiacol	40% Guaiacol, 30% Syringol, Other phenols	Manufacture food additive, pharmaceuticals	240 – 260
Creosote	Mixture of all the phenols	Manufacture binders for resins and construction works	300

* Obtained from the respective mass flow rates in the bio-oil from the Coal Tar Fractionation Unit

2.6 Markets and Economics of lignin based phenols

The markets of phenols are significantly dependent on the economics associated with supply and demand. So the selling price of a specific phenol will depend on the markets and its production economics.

2.6.1 Markets dynamics of lignin based phenols

At a market value of approximately US$1500 – US$12 000 per tonne, phenols offer a great potential for the utilisation of lignin [25]. The prices of the phenols vary due to their field of application, which is also the factor behind market demand.

From a regional perspective, the phenol market is categorised into Asia pacific, Europe, North America and rest of the world. The United States of America dominates at a market share of 30% followed by China at a market share of 27% and thereafter by Western Europe at a market share of 26% [148]. The phenol market has been on a gradual increase over the last few years due to the growing demand for its end use segment (for example in 2010 phenolic resins accounted for 70% phenol demand

worldwide) [16]. In China and Asia Pacific, their booming economies have resulted in increased demand for phenols especially in the motor and electronic industry which has in turn offset the declining growth of USA and Western Europe [13][15]. But due to the high demand of phenols in the China, these companies can only meet half of the market demand in the Asian region whilst the residual demand is imported from the rest of the world [148]. Since the market demand depends on the industry in which the phenols are used, the market prices of the phenols depend on the market value of the products manufactured in that particular industry[13]. Thus the higher the market value, the lower the market demand. This is particularly the case in the automotive, wood and electronic industry.

The market potential of lignin derived products is over US$130 billion and by 2020 it is expected to reach US$208 billion [16]. Since the current market trend and forecasts for the lignin market show the cost of lignin derived phenols are currently expensive when compared to fossil derived phenols, there is high potential to commercially produce phenols from lignin [13]. Currently there are two main constraints hindering the commercial success of lignin derived products which are namely technology maturity and interest from game changing investors. Technology maturity shows that the low yields of lignin derived products via present technologies do not allow the direct conversion into any pre-determined selection of chemicals [25]. Hence there is need to focus on chemicals with increased functional groups and also reduce the amount of unwanted by-products [39]. In order to produce aromatics, depolymerisation and extraction of pure chemical monomeric substances needs to be well controlled as it is complex to carry out due to the fact that aromatics have a tendency to quickly rearrange and form tar [11][149].

Interest from game-changing investors can change the domination of the petroleum industry as it is the major competitor of the lignin derived products. Green premium markets are now offsetting this in favour of lignin derived phenols as they are willing to pay more for bio-based products [1]. But the current decline of crude oil price further curtails research efforts of the lignin derived products [16]. As research and

development continue to contribute more into making the technology cheaper, the lignin derived products will become competitive with time [13].

Currently most aromatic products are manufactured from BTX (i.e. Benzene, Toluene and Xylene) and they represent 60 per cent of all aromatics in volume with a 100-billion-dollar market value [2][16]. Since this study is investigating the economic feasibility of lignin based phenols, phenol productions costs together with the published reports from the biomass research institutes serve as a valuable baseline during development of the models. Hence if bio-based phenols are to be competitive with fossil based phenols, the conversion of lignin into phenolic rich bio-oil and the fractionation of the phenolic rich bio-oil will need to have low production costs in order to produce market competitive products.

2.6.2 Economics of phenol plants

South Africa has abundant reserves of natural resources such as coal which in turn makes most fossil based commodities relatively cheap [9]. This in turn makes a challenging venture to build an economically viable bio-refinery in South Africa.
Economic feasibility of the biomass conversion technologies such as pyrolysis is vital for production of phenols from lignin. Studies on pyrolysis of lignin into bio-oil by Jones et al [150] have shown that it was not economically feasible to produce fuel from lignin, but production of a crude mixture of phenolic compounds was reported to have a potential to be economically feasible. This was investigated in the economic margins of producing phenol-rich pyrolysis oil (i.e. crude phenolic mixture) in the studies of Wild et al [151], where it was found to have a minimum selling price of US$1550 per tonne. This was mainly attributed to the relatively high feedstock (i.e. lignin) cost of US$650 per tonne. But the high feedstock price could be offset by selling the by-products activated carbon (market value of US$500 per tonne) and pyro-gas so as to increase the total sales volumes.

Pyrolysis of biomass also produces bio-oil which contains phenolic compounds mixed with organic acids. Techno economic studies on fast pyrolysis of biomass into

transportation fuel by Wright et al [2] showed that adoption of bio-oil as a transportation fuel is hindered by its corrosiveness. Although it may be corrosive, extraction of the phenolic compounds is another route of another route of assigning the bio-oil from pyrolysis of biomass a significant market value. This was investigated by Jazbinšek et al [25] who studied the liquid-liquid extraction of phenolic compounds from the bio-oil. It was seen that the low phenolic yields (the majority of the phenolic compounds had less than 1wt. % yield in the bio-oil) hinder effective extraction and fractionation of the phenolic compounds into fractions with higher market value. Detailed studies on the techno – economics of producing phenols from lignin are not well documented in literature, thus this report aims to answer this question if it is economically feasible to produce high market value phenolic fractions from lignin via catalytic pyrolysis.

2.7 Environmental Impact analysis

Since turn of the twentieth century industries have become more environmental conscious, determination of the environmental impact has become critical part of process design [152]. The environmental impact assessment is done through use of the Life Cycle Analysis (LCA) of the process so as to determine the hot spots of the process [153]. LCA evaluates all the stages of the process from within the boundary constraints and also the environmental aspects and the potential impacts associated with a process. The hot spots are where there is a lot of disposal from the waste stream [154]. If the process has a far less environmental impact to petroleum process, the model is then described as a green process.

Although there is no reported literature studies on LCA analysis of lignin pyrolysis processes, reported studies on biomass pyrolysis have assessed the environmental impact factor. LCA studies by Steelle et al [152] on pyrolysis of biomass into bio-oil showed that by substituting residual fuel oil with biomass based bio-oil, there was an estimated reduction in CO_2 emissions of 0.075 kg CO_2 per MJ of fuel combustion or a 70 percent reduction in emission over residual fuel oil. The bio-oil production life-cycle

stage consumed 92 percent of the total cradle-to-grave energy requirements, while feedstock collection, preparation, and transportation consumed 4 percent each. Another study by Swan et al [155] on fast pyrolysis of forest residues into bio-oil, showed that the emissions were 32.5 gCO_2-e /MJ, or a 65% reduction from the GREET 2005 petroleum gasoline baseline value (93.4 gCO_2-e/MJ).

CHAPTER 3

METHODOLOGY FOR LIGNIN PROCESS MODELLING

Figure 9 shows an algorithm that was used to develop a process model. The algorithm begins with analysis and verification of data from literature, which is used to develop mass and energy balances. This data mainly includes the feed rate from a biochemical sugarcane-lignocellulose bio-refinery, feed composition, pyrolysis temperatures and yields based on literature data. Based on the lignin processing technologies that were shown to have promise in published reports, process flow diagrams were developed that serve as the baseline for development of the Aspen Plus® models. The process flow diagrams also serve the purpose of postulating several scenarios for producing the phenolic compounds. Thereafter Aspen Plus® models are developed, based on the process diagrams. Mass and energy balances results from the simulations are then validated using literature data. An economic model is thereafter developed using the mass and energy balances and the economic assumptions. Technical and economic analysis of the developed processes is then used to determine the most economically viable process of producing phenols from lignin.

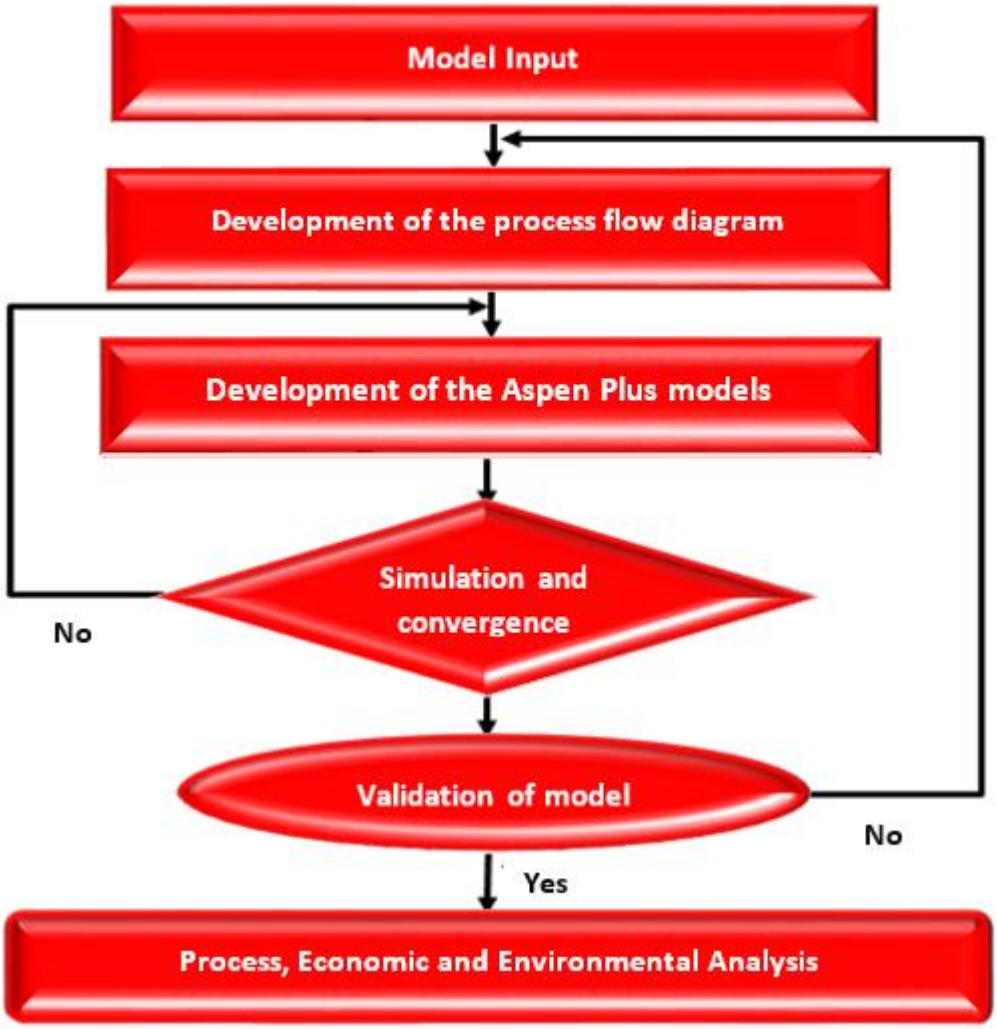


Figure 9 Algorithm for development of a model

3.1 Model Input

The required model data for simulation was compiled from published experimental results on the pyrolysis of lignin with and without catalyst. For this study, lignocellulose residue pretreatment was not considered, hence the process begins with lignocellulose residue comprising mainly of lignin that has 50 wt.% mass of free water content [27][18]. Thus, the lower boundary of the process is the lignin feed stream, whilst the upper boundaries are the phenolic streams.

The feedstock for this study is lignin residue resulting from a biochemical sugarcane-lignocellulose biorefinery at a rate of 5525 kg per hour and this was the basis of the mass and energy balances[18]. The composition of the feed was based on the averaged results obtained from literature as shown in Table 6. Due to the limited

number of articles about sugarcane lignin, articles that considered non woody lignin as feed published by Jiang et al [156], Trinh et al [92] and Lou et al [91] were used for development characterisation of model feed. The composition analysis used was the average shown in Table 6 so that the lignin of the model could be characterised in detail.

Table 6 Ultimate and proximate analysis of lignin

Lignin Type	Ultimate Analysis (Wt. % basis)					Proximate Analysis (Wt. % basis)				Reference
	C	H	N	S	O	Moisture	Volatiles	Fixed Carbon	Ash	
Wheat	62.32	5.91	0.66	-	31.11	0.05	66.00	32.24	1.67	[90]
Grass	57.80	5.70	1.20	0.14	23.60	4.7	61.2	26.7	12.1	[92]
Wheat	58.74	5.72	2.58	0.06	32.90	-	-	-	-	[91]
Bamboo	49.16	5.84	3.32	0.09	41.59	-	-	-	-	[91]
Average	42.32	5.79	1.94	0.10	49.85	2.3	63.60	29.47	9.23	

- The Ash content was used to normalise the ultimate analysis so that it could sum up to 100%.

Since the aim of this project was to determine if it is economic to produce phenols via catalytic pyrolysis of lignin, the choice of catalyst would have a significant impact on the economics of the model. The choice of the catalyst was chosen based on the cost of catalyst, regeneration temperature, thermal stability of catalyst, phenol yield and ease of recovery. Thus it was found necessary to screen the catalyst and select the two catalysts that would be used for development of various scenarios of producing phenolic compounds from lignin. Table 7 shows the catalyst screening for catalytic pyrolysis of lignin, which was based on literature data.

Table 7 Catalyst screening

Catalyst Name	cost per tonne (ZAR)	Cost ratio of Catalyst to Phenol	Catalyst Phenol conversion ratio	Economic factor (E_f)	Thermal stability of catalyst (°C)	Level of Human and Environmental Toxicology	Ease of regeneration	Reference
NaOH	4606	0.27	0.21	$1.74x10^{-5}$	320	Medium	Complex	[56]
KOH	5264	0.30	0.15	$1.74x10^{-5}$	400	Medium	Complex	[56]
TiO_2	20398	1.17	0.30	3.91	870	Low	Easy	[76]
MoO_3	12544	0.72	0.11	$4.14x10^{-5}$	795	Low	Easy	[24]
NiO	17108	0.98	0.10	$5.66x10^{-5}$	1960	High	Easy	[24]
Zeolite	9212	0.53	0.15	$3.04x10^{-5}$	2072	Medium	Easy	[24]
Fe_2O_3	10528	0.60	0.05	$3.47x10^{-5}$	1475	Low	Easy	[24]
Ru/C, Ru/Al2O3 Ru/TiO3	2632	0.15	0.12	1.51	2852	Low	Easy	[24]
NiO, CuO, MnO3, MoO3	20345	1.17	0.14	8.35	2567	High	Easy	[24]
NaOH, KOH, NaCO3	4845	0.28	0.31	0.93	250	Medium	Complex	[56]

- Prices of the catalysts and phenol were sourced from www.alibaba.com[146]

In Table 7, the ratio of cost of catalyst to the product of the cost of phenol and phenol yield is a factor (i.e. E_f) used to choose the catalyst that would be applicable to this study. This factor determines the most thermally stable with a potential for the economic viability of the process. If this number is less than 1, then the catalyst is affordable, but if the ratio is above one then the catalyst should not be considered. So the catalyst that will be suitable for the process should have an E_f value of less than one and also must be easy to regenerate as well be thermally stable. From Table 7 above the catalyst that meets the catalyst selection requirements is zeolite**.** Although other catalysts such as Fe_3O_4 had better environmental impact than zeolite, the final choice of zeolite catalyst was based on the abundant availability of phenolic yield-temperature data that enables determination of the robustness of the model. The catalyst is impregnated into the lignin and thereafter the lignin particles are pyrolysed. Zeolite catalyst has a density of 600 – 860 $kg.m^{-3}$, lignin has a density of 1200 – 1230

kg.m^{-3}, pyrolysed lignin has a density of 0.45 kg.m^{-3} and the fluidisation media which is usually sand has density of 1500 – 1650 kg.m^{-3} [157][158]. Thus it can be seen that when the lignin particles are fully pyrolysed, they are become sufficiently small and light to escape via the cyclone separator together with the embedded catalyst particles. The deactivated catalyst is sent to the combustor where char is burnt off. This regenerates the catalyst so that it can be recycled back to the reactor while the released energy can be used to meet some of the utility requirements of the plant.

Another option is using a cheap catalyst that can be disposed of together with the pyrolysis char product, thus avoiding the need of a recycle stream. From Table 7, it can be seen that the catalysts that suits this scenario is NaOH based on the selectivity towards monomeric phenols and low market price. The articles in Table 7, used lignin-catalyst ratio ranging from 1:1 to 1:10. In all these studies it was noted that there was a significant difference in increase of yield of the phenolic compounds at various lignin-catalyst ratios. Thus it was decided to use the minimum catalyst-lignin ratio of 1:5 which will minimise cost of catalyst.

3.2 Development of process flow diagrams

Process diagrams indicate the flow plant processes and the relationship between unit equipment. In the case of this study, the flowsheet comprises of the catalytic lignin pyrolysis plant, which produces the phenol rich bio-oil, and the phenol fractionation plant, which separates the crude phenolic mixture into fractions of phenols.

Based on the two selected catalysts, four scenarios for process and economic analysis were selected as the technological pathways for conversion of lignin into phenolic products. Scenarios 1 and 2 are about producing a crude phenolic mixture called creosote from lignin via catalytic pyrolysis of lignin, whilst scenarios 3 and 4 are about producing phenolic fractions via fractional distillation from the crude phenolic mixture (i.e. creosote) produced from catalytic pyrolysis of lignin. Scenario 1 uses a relatively cheap catalyst NaOH for catalytic pyrolysis of lignin whilst scenario 2 uses relatively expensive catalyst zeolite. Scenario 3 uses the phenolic mixture from catalytic

pyrolysis of lignin using NaOH to produce phenolic fractions whilst scenario 4 uses the phenolic mixture produced from catalytic pyrolysis using zeolite catalyst.

Scenario 1: Production of crude phenol solution (creosote) from lignin using sodium hydroxide, which is not recovered from the char product, as shown in Figure 10. The process begins with lignin impregnated with the catalyst being fed into the pyrolysis reactor where lignin decomposes into char, vapours and gases. Vapours condense into phenol solution (i.e. creosote) in the condenser whilst non-condensable gases escape to the combustor where they are burnt to provide energy for the reactor and utilities.

Since the char is embedded together with catalyst and ash, costing it so as to sell it as activated carbon is a challenge as it has to go thorough further refinement. This bio-char has a high ash content (25% total mass) mainly due to the embedded sodium hydroxide catalyst and lignin ash. If the resulting char is to be sold as an energy product, the ash content has to be as low as possible. But sodium is one of the main fluxing ingredients for the making of glass. In glass making, sand is mixed with several fluxing ingredients such as sodium hydroxide, calcium oxide and is thereafter melted in furnace to form glass. Fluxing agents mainly composed of group 1 and 2 elements are used to lower the melting temperature of silica. Studies on the future and challenges of glass making industry by Pellegrino et al [159] showed that the major challenges of glass making are reduction in energy consumption during melting (half of the energy of the plant is used for melting) and also reduction of green-house gas emissions. Currently energy demands for glass making are met by using natural gas and electricity to melting purposes. In order to meet these energy demands, glass makers currently use 80% natural gas, 17% electricity and 3% from fuel oil and other sources [160]. So if the char/sodium hydroxide mixture can be sold to glass makers at the average market price based on the composition in the mixture, it will assist in alleviating the energy demands of this industry. Lignin ash is mainly composed of silicon dioxide (a major component for glass making) and minor amounts of oxides of potassium, sodium, calcium. Since oxides of sodium, potassium and calcium are used

as fluxing agents, there is no need to separate lignin ash from the spent sodium hydroxide catalyst. The mixture of sodium hydroxide and silicon dioxide is called sodium silicate. Sodium silicate has market price of US$ 200 – 500 per tonne and biochar has market price of US$ 149 per tonne [161]. In order for the plant to remain energy self-sufficient, the non-condensable gases are burnt together with a fraction of the char. The residual char/sodium oxide mixture is then sold to glass makers.

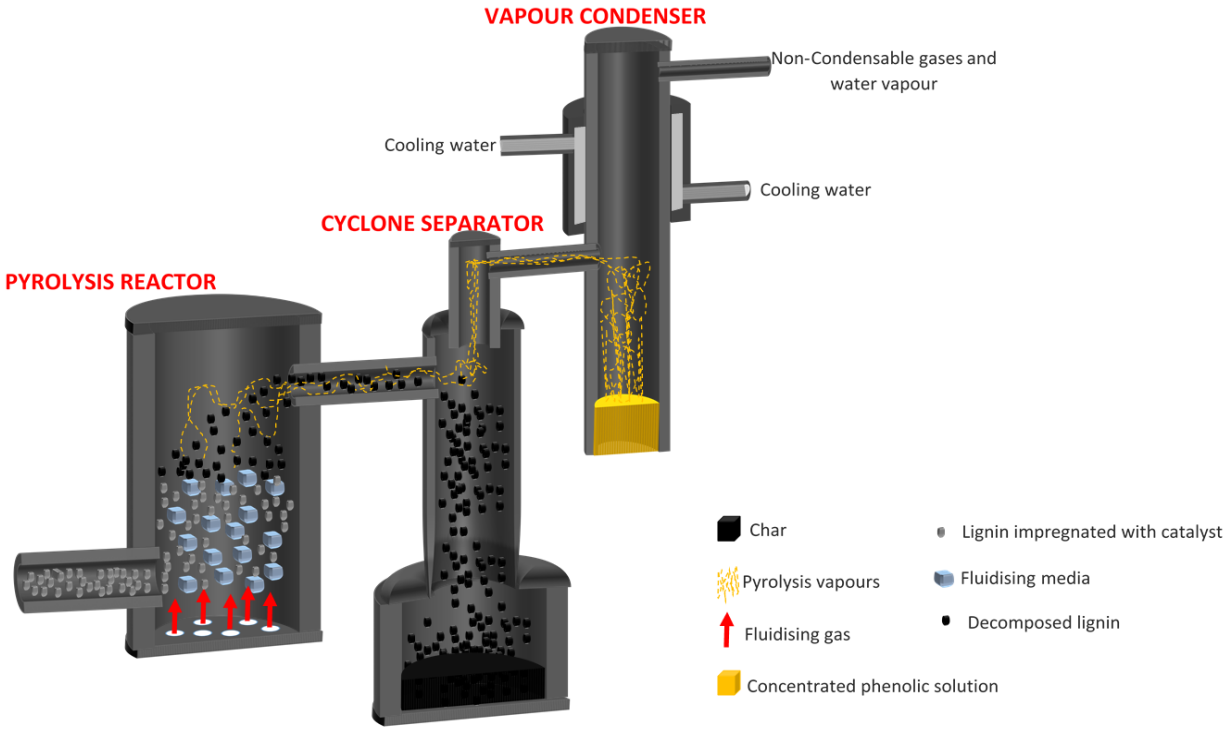


Figure 10 Catalytic pyrolysis of lignin into a crude phenolic mixture using sodium hydroxide

Scenario 2: Production of crude phenol solution (creosote) from catalytic pyrolysis of lignin using a zeolite catalyst, which is thereafter recycled back to the reactor, as shown in Figure 11. The process is the same as scenario 1 where lignin is converted into a crude phenolic solution (i.e. creosote) but the catalyst that is used in this case is zeolite. Just as in scenario 1, the char exits the reactor embedded together with the ash and catalyst. But since the catalyst has a higher market value than that of scenario 1, it has to be recovered by combusting all the char off the catalyst. The energy produced from combustion of char meets all the energy demands of the reactor whilst the excess energy is sold back to the sugarcane biorefinery as an energy product that

preheats the utilities through in heat exchangers. Since pyrolysis gas is not pure natural gas, it is sold as untreated natural gas at the price of gas well natural gas US$1.5 per thousand cubic metre [162].

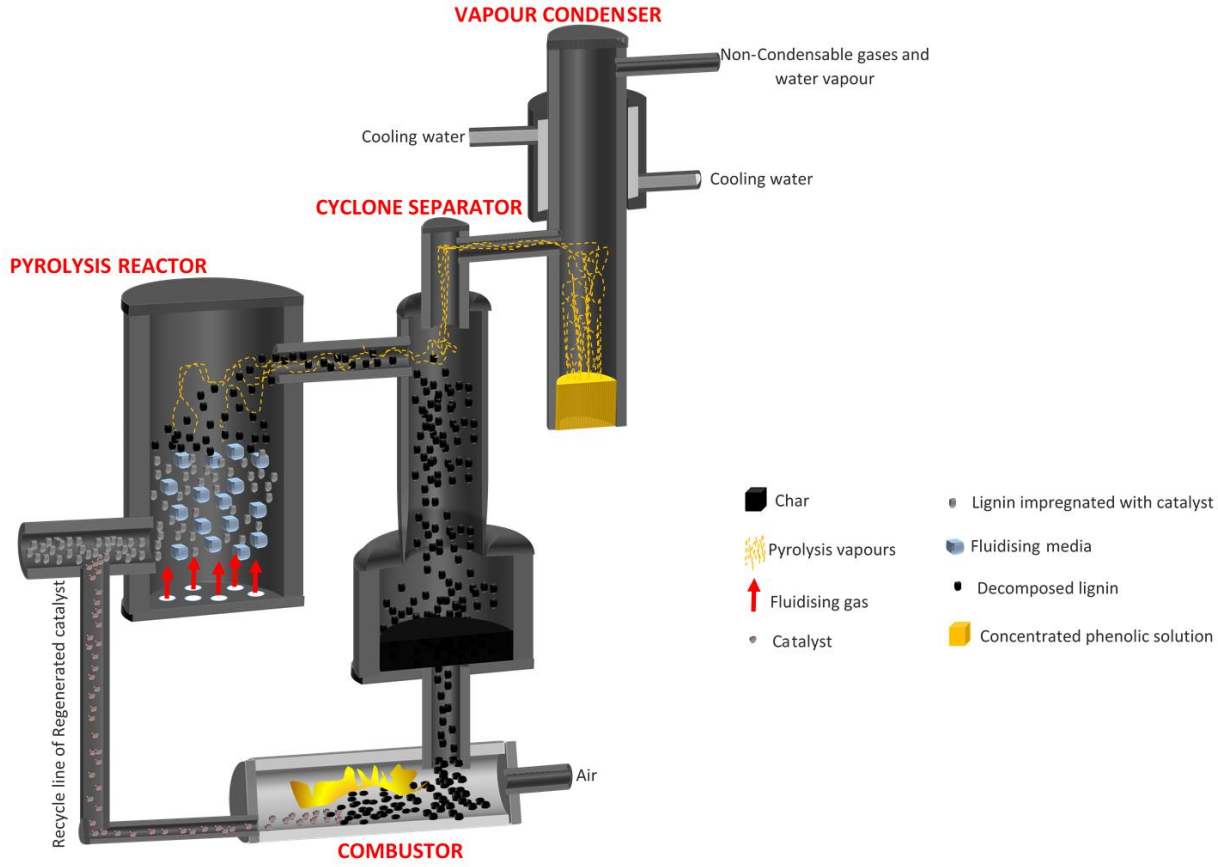


Figure 11 Catalytic pyrolysis of lignin into a crude phenolic mixture using zeolite catalyst

Scenario 3: Production of phenolic fractions using relatively a low value catalyst which is thereafter disposed of as shown in Figure 12. The process first converts the lignin into a phenolic mixture just as described in scenario 1 and thereafter, the crude phenolic mixture is fractionated into phenolic fractions in the fractionation column. Just as in the scenario 1, the char has high ash content but in this scenario all the gas and char have to combusted so as to meet the energy demands of the plant. In order to meet the energy demand of the whole plant, energy is imported from the sugarcane biorefinery. The resulting mixture is a sodium hydroxide/lignin ash mixture with a composition of 8 wt. % mass lignin ash and sodium hydroxide 92 wt. % mass. As

mentioned in scenario 1, this mixture is called sodium silicate which can be used in glass making.

The average boiling point of the crude phenolic mixture ranges from 200 – 250°C depending on the composition [39][139]. Thus at the operating temperature of the fractionation column is dependent on the boiler duty.

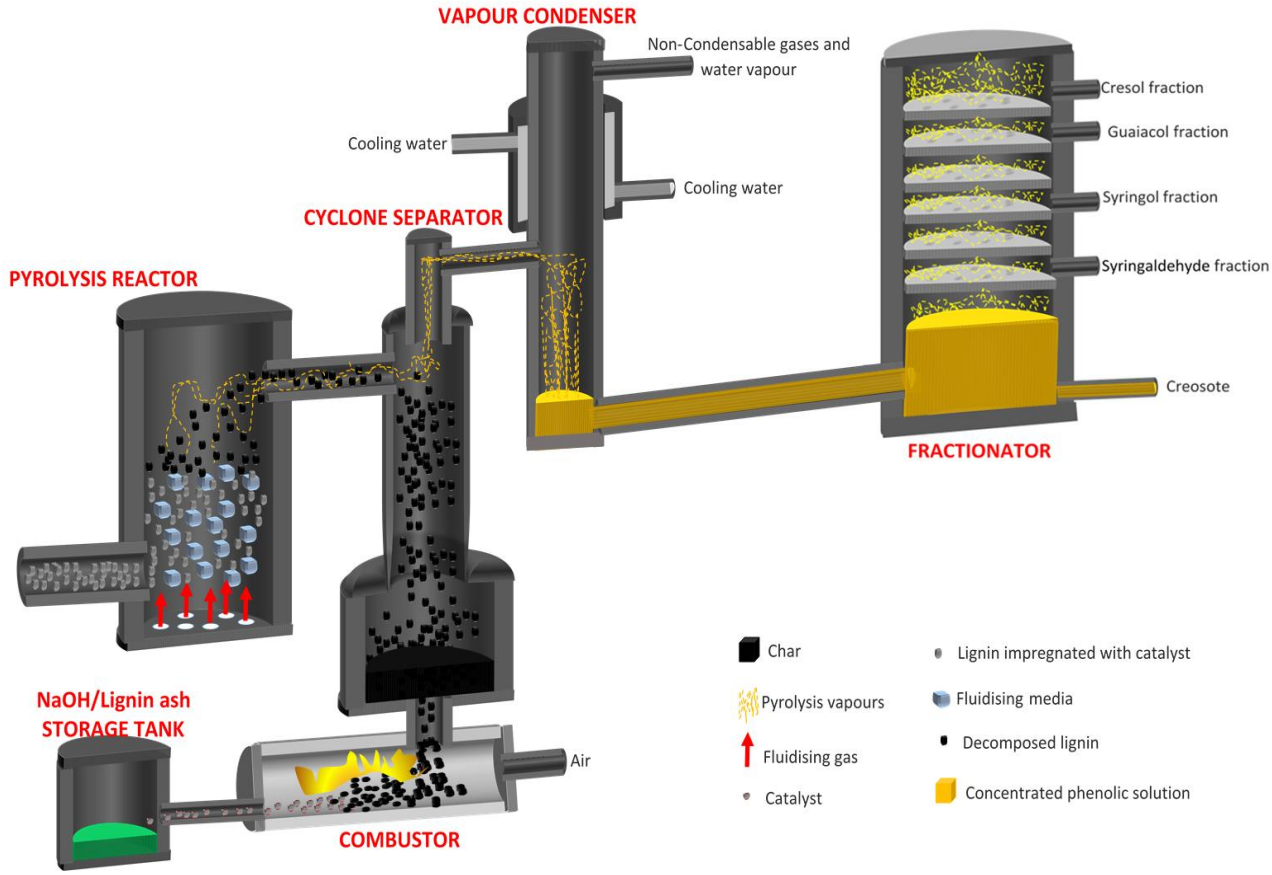


Figure 12 Fractionation of crude phenolic mixture from catalytic (NaOH) pyrolysis of lignin

Scenario 4: Production of phenolic fractions using a high market value catalyst (zeolite), which is recycled back to the reactor as shown in Figure 13. This scenario fractionates the crude phenolic mixture that is produced via catalytic pyrolysis of lignin using zeolite catalyst just as described in scenario 2. In order to meet some of the energy demands of the plant, char is combusted off the catalyst-ash mixture and this also enables separation so that the catalyst can be recycled back to the pyrolysis

reactor. In order to meet the energy demand of the whole plant, energy is imported from the sugarcane biorefinery.

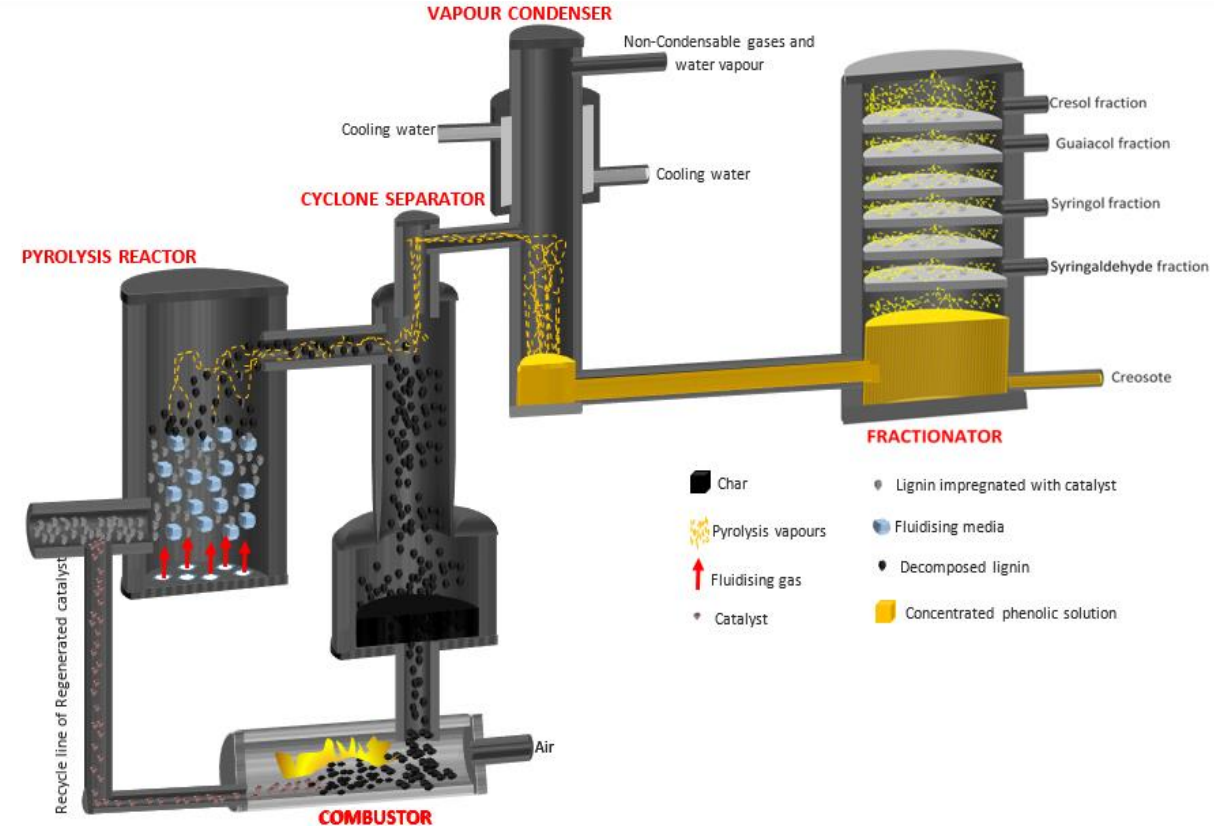


Figure 13 Fractionation of crude phenolic mixture from catalytic (Zeolite) pyrolysis of lignin

3.3 Development of the Aspen Plus models

Modelling is a process where a physical system is described by appropriate mathematical equations that are executed in a computational technique (such as Aspen Plus®) in order to predict the system behaviour [141][94]. Computational techniques such as Aspen Plus® execute the models based on user specification thus the predicted results will depend on the quality of data used for input [163]. Engineering software packages such as Aspen Plus® enable processes to be simulated so as to determine various parameters such as the mass and energy balances and economic viability of a process [141]. Aspen Plus® has a database composed of components for petro chemistry and also other inorganic components. However components of bio-processes such as lignin are usually not found in it, hence the user

has to define the components using the User Defined tool and also methods such as HCOALGEN, DCOALIGT, PROXANAL, ULTANAL, and SULFANAL[164][165].

There are two main methods of simulating fast pyrolysis of lignin, namely kinetic modelling and mathematical modelling[141][166][167]. Kinetic modelling involves development of a model based on the kinetics of a process. Since pyrolysis is a complex process with multiple possible reaction pathways, prediction of the product spectra of the lignin pyrolysis model would require an extensive amount of data such as radicals formation and kinetic constants for every reaction pathway [100][168]. Mathematical modelling is the simpler, more robust route as it involves using simplified mathematical models based on chemical reactions and process parameters such as yield [7][141].

In literature, there are simple Aspen Plus® and molecular models of lignin pyrolysis such as those reported by Peter et al [94] and Avni et al [149], which are mainly based on the kinetics of the process. Process optimisation using these models is a rather cumbersome process, as it requires extensive amounts of data and mathematical models that relate the kinetics to process parameters. Studies by Lestinsky et al [169] also revealed the shortcomings of such existing Aspen Plus® models, in terms of predicting the product spectra of lignin pyrolysis at commercial scale, and process optimisation.

Since pyrolysis is a very complex process, accurate modelling requires detailed information about the kinetics, feed and products composition. Ranzi et al [23] published detailed kinetics on pyrolysis of lignin into phenols (*i.e. mainly for fast and vacuum pyrolysis*). The series reactions shown in pyrolysis temperatures mainly due to the complex reaction pathways of lignin pyrolysis.

Table 8 are primary and secondary reactions that occur during lignin pyrolysis and their respective enthalpies. But if these equations are to be considered for the modelling of the reactions occurring in the pyrolysis reactor so as to develop the mass and energy balances, additional data is required. Such data is in the form of free radical reactions,

reaction pathways at various temperatures and by-product spectra. Such data would be needed for balancing the complex stoichiometric equations. As this data is not available in published literature, application for the development of pyrolysis model for this study is not feasible. Also balancing the stoichiometric equations becomes complex at different pyrolysis temperatures mainly due to the complex reaction pathways of lignin pyrolysis.

Table 8 Multistep kinetic models of lignin models [23]

Reaction	Rate of reaction equation (s^{-1})	Heat of Reaction [$kJ.kg^{-1}$]
LIG-C → 0.35 $C_{15}H_{14}O_4$ + 0.1 $C_9H_{10}O_2$ + 0.08 PHENOL + 0.41 CH_4 + H_2O + G[COH_2] + 0.495 CH_4 + 0.32 CO + 5.735 Char	+ 4x10 ^{15} .e $^{(-48500/RT)}$	-100
LIG-H → LIGOH + C_3H_6O	+ 2x10 ^{13} .e $^{(-37500/RT)}$	130
LIG-O → LIGOH + CO_2	+1x 10^9.e $^{(-25500/RT)}$	260
LIGCC → 0.3 $C_9H_{10}O_2$ + 0.2 PHENOL + 0.35 HAA + 0.7H_2O + 0.65 G[CH_4]+ 0.6 G[C_2H_4]+ G[COH_2]+ 0.4 G[CO]+ 0.4 CO + 6.75 Char	+5x 10^6.e $^{(-31500/RT)}$	450
LIGOH → LIG + 0.15 G[H_2] + 0.9 H_2O + 0.5 CH_3OH + 0.5 G[CH_3OH] + 0.05 CO_2 + 0.3 CO + G[CO] + 0.05 HCOOH + 0.6 G[COH_2] + 0.45 G[CH_4] + 0.2 G[C_2H_4] + 4.15 Char	+3 x 10^8.e $^{(-30000/RT)}$	70
LIGOH → 1.3 G[H_2] + 1.5 H_2O + 0.5 CO_2 + 1.6 G[CO] + 3.9 G[COH_2]+ 1.45G[CH_4] + 0.7 C_2H_4 + 10.15 Char	+1 x 10^2.e $^{(-15000/RT)}$	-1300
LIG → 0.95 H_2O + 0.2 CH_2O + 0.2 C $_2H_4O$ + 0.4 CH_3OH + CO + 0.2 C_3H_6O + 0.6 G[CH_4] + 0.65 G[C_2H_4] + 0.05 HCOOH + 0.45 G[CO] + 0.5 G[COH_2] + 5.5 Char	+1 x 10^9.e $^{(-30000/RT)}$	-300
LIG → G[CH_4] + 0.5 G[C_2H_4] + 0.4 G[H_2] + 0.6 H_2O + 0.4 CO + 0.4 CO_2 + 0.2 G{CO} + 2 G[COH_2] + 6 Char	0.25.T.e $^{(-8000/RT)}$	-1770
LIG → FE2MACR	8.T.e $^{(-12000/RT)}$	890

It was recommended by Lestinsky et al [169] that industrially suitable models would need to be able to predict the product spectra at any operating parameter. Thus for this study, a novel Aspen Plus® lignin pyrolysis model was developed as a combination of kinetic and parametric data, based on process parameters and chemical reactions of the product components [141][170]. Reported data on non-catalytic and catalytic pyrolysis of lignin can be found in literature in the form of yield versus temperature trends. These trends enable the product spectra of lignin pyrolysis to be predicted at

any temperature, thus it was decided to develop parametric equations based on this temperature- yield data so as to enable the Aspen Plus® models accurately predict the product spectra of lignin pyrolysis. As fast pyrolysis is associated with high heating rates, it was assumed that the effect of change of heating rate does not significantly affect the phenolic yield at high heating rates (i.e. >900^{o}C per minute) [171][69].

Since this study is about catalytic pyrolysis of lignin, the yield-temperature data is used to predict the product distribution of non-catalytic pyrolysis of lignin and thereafter the product spectra of non-catalytic pyrolysis of lignin is used to predict the product spectra of catalytic pyrolysis of lignin based on the kinetics of the catalyst. The sugar mill lignin residue is composed of grass type of lignin, thus it was decided to develop the parametric equations using articles that had this type of lignin. The temperature-yield data is found in non-catalytic pyrolysis of lignin articles published by Jiang et al [90], Trinh et al [92], Zhang et al [172] and Min et al [37]. The methodology of developing the parametric equations is illustrated in Figure 14. The yield-temperature data of the products of lignin pyrolysis were plotted for each product constituent and the parametric equations were then derived through statistical analysis of the scatter plots using ANOVA.

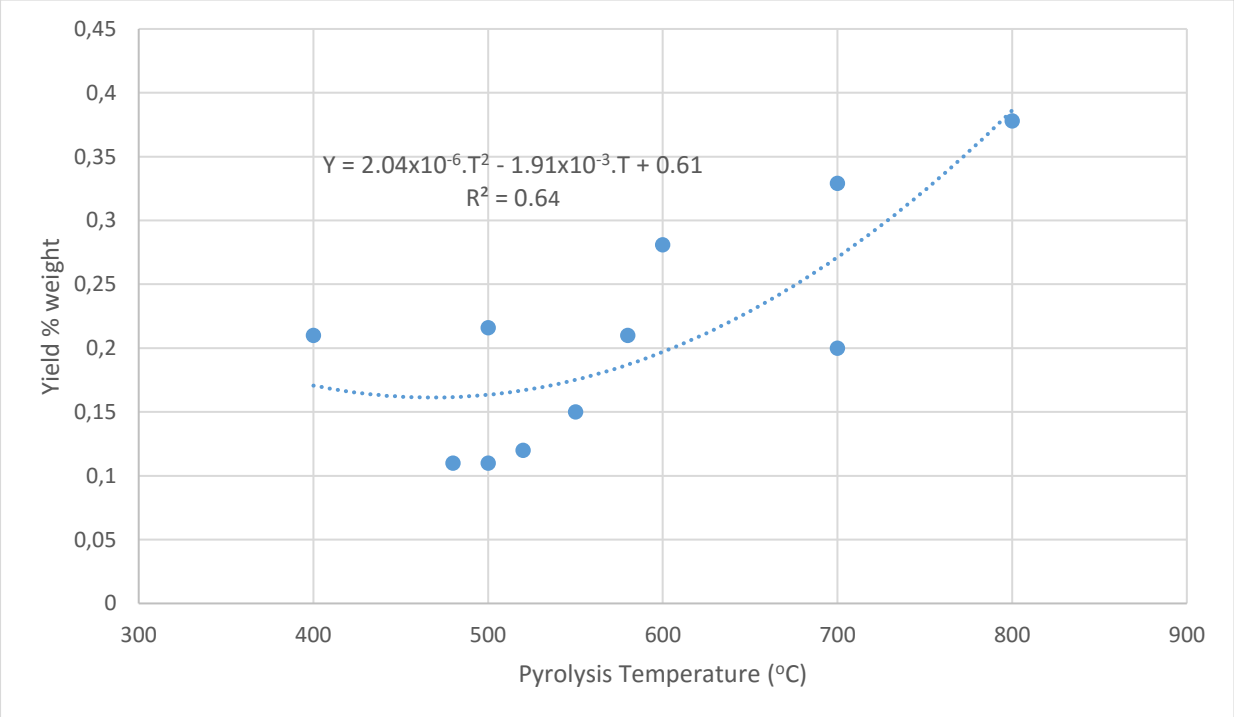


Figure 14 Yield Temperature graph showing the parametric equation of phenol [91][90][92]

Based on this data, and the methodology illustrated in Figure 14 the parametric equations of products from non-catalytic pyrolysis of lignin are summarised in Table 9. Equations in Table 9 are deemed valid if the scatter of the data points had to be spread over the whole temperature range and the regression coefficient is high enough to be almost one as illustrated in the example shown in Figure 14.

Table 9 Stoichiometric and parametric equations of the phenols and gases for lignin pyrolysis

Stoichiometric equation	Parametric Equation	Compound name	Reference
Non condensable gases and water			
$C + O_2 + O_2 \rightarrow CO_2$	$Y = -2.86x10^{-5}.T^2 + 5.2x10^{-2}.T - 15.48$, $R^2 = 0.99$	Carbon dioxide	[171]
$C + 2H_2 \rightarrow CH_4$	$Y = -3.75x10^{-6}.T^2 + 9.12x10^{-3}.T - 0.25$, $R^2 = 0.97$	Methane	[171]
$2H_2 + O_2 \rightarrow 2H_2O$	$Y = -2.92X10^{-5}.T^2 + 5.13x10^{-2}.T - 13.08$, $R^2 = 0.99$	Water	[171]
$2C + O_2 \rightarrow 2CO$	$Y = 5.71x10^{-6}.T^2 + 1.27x10^{-2}.T - 5.42$, $R^2 = 0.97$	Carbon monoxide	[171]
Phenolic compounds			
$6C + 3H_2 + 0.5O_2 \rightarrow C_6H_5OH$	$Y = 2.04x10^{-6}.T^2 - 1.91x10^{-3}.T + 0.61$, $R^2 = 0.64$	Phenol	[91][90][92]
$6C + 5/2H_2 + 0.5O_2 \rightarrow C_6H_4OH$	$Y = -4.00x10^{-7}.T^2 + 8.56x10^{-4}.T - 0.22$, $R^2 = 0.96$	P-Cresol	[91][90][92]
$7C + 4H_2 + O_2 \rightarrow C_7H_8O_2$	$Y = -6.61x10^{-6}.T^2 + 5.49x10^{-3}.T - 1.12$, $R^2 = 0.62$	Methoxyphenol	[91][90][92]
$8C + 4H_2 + 1.5O_2 \rightarrow C_8H_8O_3$	$y = -3.95x10^{-6}xT^2 + 4.85x10^{-3}.T - 1.15$, $R^2 = 0.61$	Vanillin	[91][90][92]
$7C + 4H_2 + 0.5O_2 \rightarrow C_7H_8O$	$Y = -6.4x10^{-8}.T^2 + 2.48x10^{-4}.T - 0.06$, $R^2 = 0.72$	O-Cresol	[91][92][86]
$10C + 6H_2 + O_2 \rightarrow C_{10}H_{12}O_2$	$Y = 1.21x10^{-5}.T^2 - 1.39x10^{-2}.T + 4.15$, $R^2 = 0.97$	Eugenol	[91][90][92]
$7C + 4H_2 + O_2 \rightarrow C_7H_8O_2$	$Y = -2.57x10^{-6}.T^2 + 3.07x10^{-3}.T - 0.44$, $R^2 = 0.65$	Guaiacol	[91][90][92]
$6C + 3H_2O_2 \rightarrow C_6H_6O_2$	$Y = -3.66x10^{-6}.T^2 + 5.50x10^{-3}.T - 1.20$, $R^2 = 0.62$	P-Hydroquinone	[91][90][92]
$8C + 5H_2 + 1.5O_2 \rightarrow C_8H_{10}O_3$	$Y = -2.24x10^{-6}.T^2 + 2.79x10^{-3}.T - 0.71$, $R^2 = 0.69$	Syringol	[91][90][91]
$8C + 4H_2 + 0.5O_2 \rightarrow C_8H_8O$	$y = -7.71x10^{-7}.T^2 + 6.98x10^{-4}.T - 0.02$, $R^2 = 0.99$	Desaspidinol	[91][92][86]
$6C + 3H_2 + 1.5O_2 \rightarrow C_6H_6O_3$	$Y = -2.79x10^{-6}.T^2 + 5.11x10^{-3}.T - 1.52$, $R^2 = 0.75$	Catechol	[91][90][92]
$9C + 5H_2 + 2O_2 \rightarrow C_9H_{10}O_4$	$Y = -3.29x10^{-6}.T^2 + 3.26x10^{-3}.T + 0.04$, $R^2 = 0.88$	Syringaldehyde	[91][90]
$9C + 5H_2 + O_2 \rightarrow C_9H_{10}O_2$	$Y = -2.28x10^{-5}.T^2 + 2.55x10^{-2}.T - 2.94$, $R^2 = 0.89$	Vinyl guaiacol	[91]
$9C + 5H_2 + 1.5O_2 \rightarrow C_9H_{10}O_3$	$Y = -4.21x10^{-7}.T^2 + 5.60x10^{-4}.T - 0.034$, $R^2 = 0.80$	Acetovanillone	[90][92]
$10C + 6H_2 + 2O_2 \rightarrow C_{10}H_{12}O_4$	$Y = -3.47x10^{-6}.T^2 + 3.53x10^{-3}.T - 0.09$, $R^2 = 0.96$	Acetosyringone	[90][92]
Oligomers			
$15C + 8H_2 + O_2 \rightarrow C_{15}H_{16}O_2$	$Y = 0.082.T - 21.05$; $R^2 = 0.71$	Bis-phenol	[86] [173]

**Parametric equation for pyrolysis conversion within a temperature range 400 - 800^oC*

The product spectra of non-catalytic pyrolysis of lignin that is predicted using the parametric equations in Table 9 is used to predict the product distribution of catalytic

pyrolysis of lignin based on the kinetics of zeolite and sodium hydroxide catalysts. These kinetics are the activation energy, reaction constants which are summarised in Table 10 and the lignin reaction pathways in the studies of Faravelli et al [104] and Nuemman et al [84].

Table 10 Kinetics of the sodium hydroxide and zeolite catalysts [174][175]

Sodium hydroxide catalyst			**Zeolite catalyst**		
Order of reaction	Reaction constant (min^{-1})	Activation energy($kJ.mol^{-1}$)	Order of reaction	Reaction constant (min^{-1})	Activation energy ($kJ.mol^{-1}$)
1	$4.5x10^{-2}$ – $5.6x10^{-4}$	34.3 – 39.7	1	$6.8x10^{-2}$ - $6.6x10^{-4}$	47.9 -54.2

Aspen Plus® has three types of reactor models that can be considered for the pyrolysis of lignin. They include:

1. *Balance conversion* reactors – these include the RSTOIC and the RYIELD. The RSTOIC utilises stoichiometric equations of the components, whilst the RYIELD reactor utilises yield values of the components in order to model the process [170]. These reactors are mainly used for predicting mass and energy balances. In these reactor models, the user specifies the conversion or yield and Aspen Plus® then runs the simulations based on user specifications to produce the mass and energy calculations [141][167].

2. *Equilibrium reactors* - these include the REQUIL and the RGIBBS. The REQUIL utilises equilibrium reactions whilst the RGIBBS utilises the minimum Gibbs energy of the reactions in order to model the process [167][170]. These models are suitable for fast equilibrium reactions. However the RGIBBS is more flexible as it handles multiple phases through use of the Gibbs free energy minimisation. The only drawback is that it requirement of accurate thermodynamics since Gibbs energy is calculated from enthalpy and entropy [3][65][7].

3. *Rate based kinetic reactors* - these include RBATCH, RCSTR, and RPLUG. The RSTOIC and the RPLUG are used for rigorous simulations as allow the many variables to be incorporated such as dimensions, etc.[2][5]. When reaction kinetics are well known,

these models will work quite well. The RBATCH is usually used for less rigorous simulations.

Since predicting the product spectra of catalytic pyrolysis of lignin using stoichiometric equations in Table 8 was found to be not feasible mainly due to unavailability of the data required to balance the stoichiometric equations, it was decided to model lignin pyrolysis using the RYIELD, RSTOIC and the RCSTR reactor blocks that enable use of yield-temperature equations in Table 9 and the kinetics of the catalysts shown in Table 10.

The developed simulation of catalytic pyrolysis of lignin is shown in Figure 15. Model development begins with selection of compounds that are associated with lignin pyrolysis shown in Table 9 into the database of the pyrolysis Aspen Plus® model and thereafter a thorough property and binary parameter analyses was performed using the Aspen Plus® property estimation and binary run functions. The UNIQAUC-DMD property estimation method for VLE development was applied, as the Dortmund databank is the most advanced and recently updated databank in the software. Binary interaction parameters were estimated for all of the conventional components in the simulation, including the user-defined lignin. In Aspen Plus® based on the selected components, stream classes are MIXED components, conventional inert solid (CISOLID) components or Non-Conventional (NCPD) components [170][134]. CISOLID is applied to represent components in solid state during reactions whilst MIXED represents components take part in phase equilibrium calculations (Aspen Technology) [141]. NCPD are user defined components that are not available in the Aspen Plus database which are defined by inserting the ultimate and proximate analysis data for determination of the enthalpy and density of the user defined component.

The developed catalytic lignin pyrolysis models (shown in Figure 15 and Figure 16) comprise of three reactor blocks that represent what is occurring within the pyrolysis reactor, two separator blocks, a drier and a char combustor. DRIER is an RSTOIC

reactor that serves the purpose of drying the catalyst lignin mixture to the required pyrolysis feed moisture content of less than 10 wt.% lignin. DECOMP is the RYIELD reactor block which serves the purpose of splitting the lignin into its constituent elements based on its proximate and ultimate analysis. This was done so that the stoichiometric equations of the product components of lignin pyrolysis shown in Table 9 could be incorporated into the PYROLYSI block where the products of pyrolysis reactions are modelled. PYROLYSI is the block RSTOIC serves the purpose of predicting the product distribution of lignin pyrolysis using the stoichiometric equations and the parametric equations shown in Table 9. The parametric equations are inserted into the calculator block of the RSTOIC block so that the software could automatically determine the mass flowrates of the product components at temperatures 400 – 800^{o}C. Products of the non-catalytic pyrolysis of lignin from the block PYROLYSI are fed into the reactor block CATALYS where products of catalytic pyrolysis of lignin are predicted based on the reaction pathways of Nuemman et al [84] and Zakzeski et al [42], and activation and reaction constant shown in Table 10. Products from the catalytic pyrolysis block are sent to the SEP1 and SEP2 blocks (flash drums) where the solids are separated from the vapours and also the condensed phenols from non-condensable gases. COMBUST is RSTOIC reactor block that serves the purpose of burning the char and the gases. In this study, lignin was modelled as a non-conventional component (NCPD), char and ash as solid component (CISOLID) and rest of the components (moisture) were modelled as mixed components (MIXED).

Since pyrolysis is dependent on several factors, the following assumptions were made:

1) Lignin ash is mainly made up of SiO_2, thus the SiO_2 component used in Aspen Plus to represent ash[92].
2) There is complete combustion in the combustion block COMBUST.
3) There is no heat loss around and between the block.

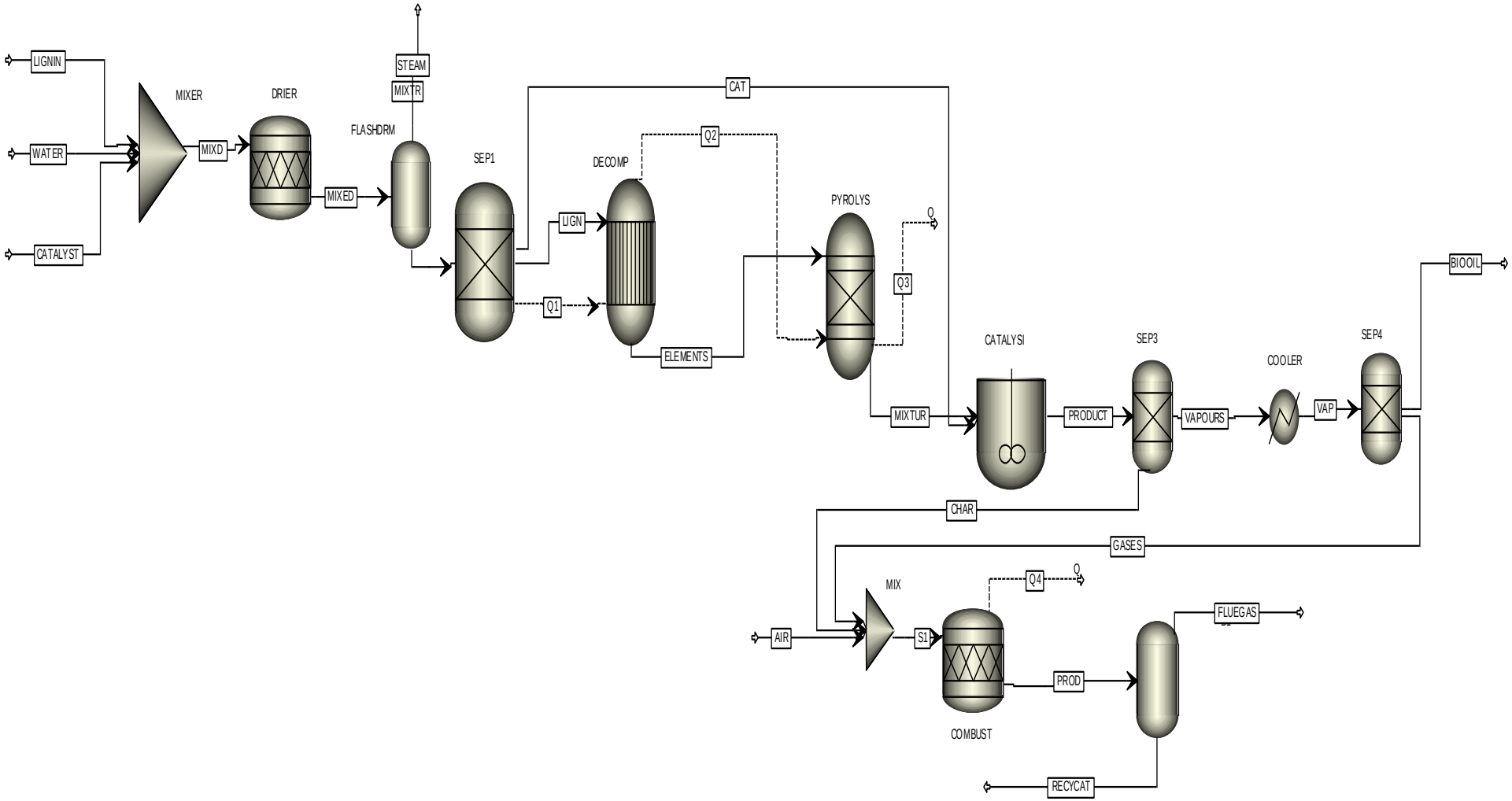


Figure 15 Catalytic Lignin pyrolysis model implemented in Aspen Plus

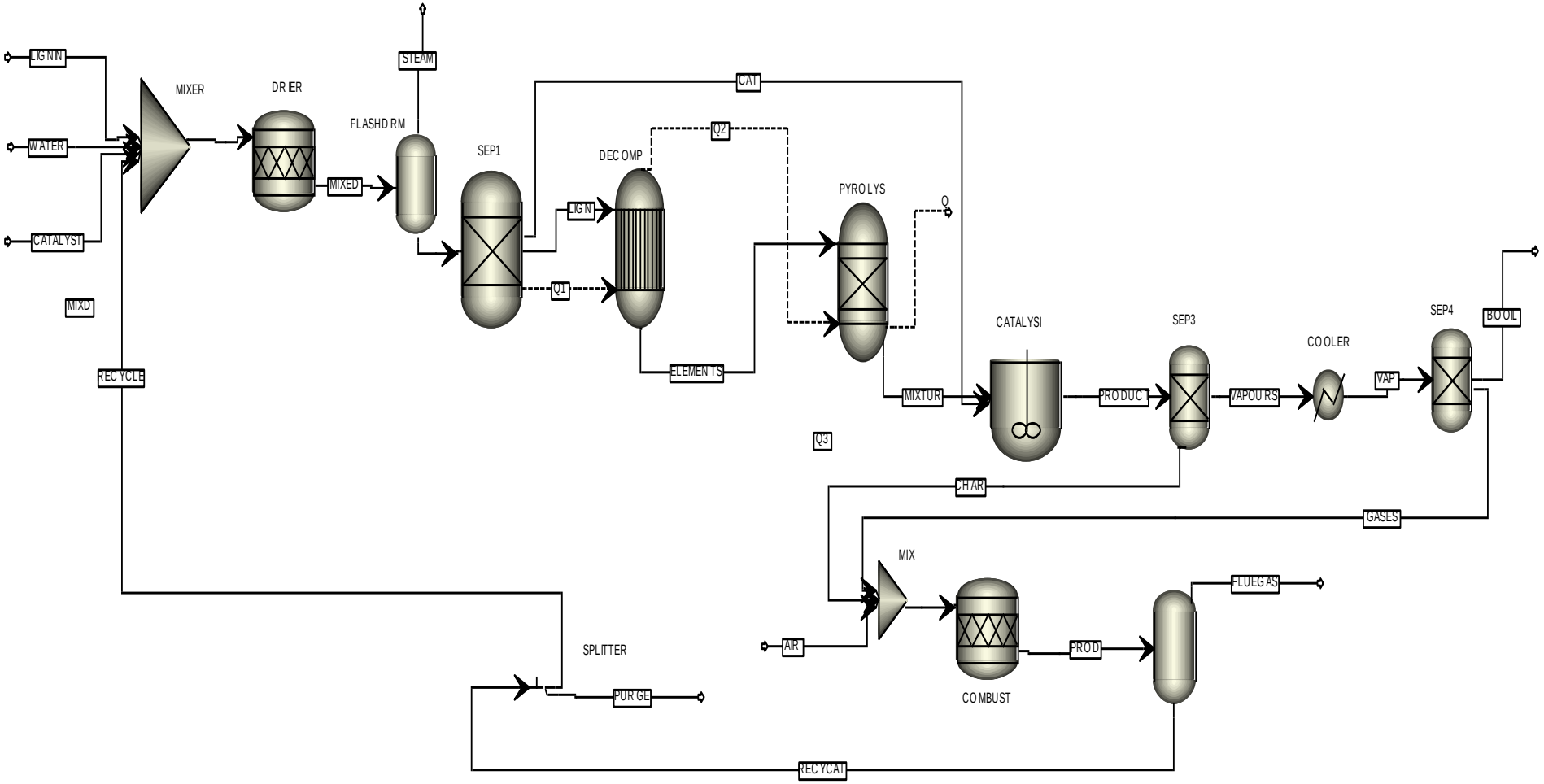


Figure 16 Catalytic lignin pyrolysis model with catalyst recycle

In the case of fractionation of the phenolic mixture, Aspen Plus® has several distillation columns that can be employed namely Petrofrac, Redfrac and Mutlifrac columns. Since fractionation of the phenolic mixture is based on the simulation studies of coal tar distillation, Aspen Plus® fractionating columns used in coal tar modelling were selected. Simulation studies by Wright et al [2], Holland et al [137] and Bravo et al [142] used the Petrofrac column that as required the least amount of input for predictions of the phenolic fraction compositions.

Since modelling fractional distillation using software such as Aspen Plus® requires the user to specify minimum inputs necessary for the generation of the mass and energy balances, defaults specifications of Aspen Plus® of parameters such as distillate rate, reflux ratio and distillate to feed ratio are preferably used as initial specifications for the distillation columns. Aspen Plus® user tools are then employed as shortcut methods for determination of the optimum operating parameters needed for production of targeted phenolic fractions shown in Table 5. One of these tools that is frequently used in process modelling is the Design Specification tool [94][142]. The Design Specification tool uses any of the variable of the feed stream or process unit in order to meet specified design parameters by employing multi component distillation short cut methods such as the Fenske equation and the Gilliland correlation [141][166].

When simulating multi-component distillation, the user needs to first specify the following based on specified Aspen Plus® default values;

- *Feed*: It is calculated by an upstream module from the pyrolysis plant.
- *Operating pressure*: The operating pressure affects the relative volatility of the phenolic compound thus it has an effect on the extent of separation of the components [7][169]. It also has an effect on the economic performance of the distillation column mainly due to the increase of costs as the pressure of the column increases [2]. Thus it is rather preferable to operate at 1 bar as it reduces the costs and also the boiling points of phenolic compounds still differ enough to enable separation.

- *Number of trays*: Aspen Plus® does not design a process but rather uses the input specifications from the user, it is then necessary for one to know the anticipated output so as to determine if the prediction of the model is accurate[2][141]. One way is using the Fenske equation to determine the minimum number of trays (Aspen Plus® recommended 20 trays for this study), which are then set as the initial specification before employing the Aspen Plus® design specification tool to run iterations with varying number of trays until the product specification is met. The Fenske equation:

$$Nmin = \log\{\left[\frac{(Xi,n+1)}{Xi}\right].\left[\frac{Xj,1}{(Xi,n+1]}\right].\frac{1}{\log(\alpha i,j)} \qquad \textit{Equation 4}$$

Where: N_{min} – Minimum number of trays

X – Molar fraction of components i, j in the liquid phase

$\alpha_{i\,j}$ - The relative volatility between components i and j

- *Reflux ratio*: Reflux Ratio is the ratio of the liquid that has returned to the distillation column to the amount of liquid removed [139]. The calculation of the Reflux Ratio includes the composition of vapour pressure that is leaving the plate. In the model, the optimum reflux ratio for the current column simulation model is used to specify the column energy balance. It is usually tied to a product stream purity as it affects the distillate composition.

$$Rmin + 1 = \Sigma\left[\frac{(\alpha i,HK.\ X,i)}{(\alpha i,HK-\theta)}\right] \qquad \textit{Equation 5}$$

Where: R_{min} – Minimum reflux ratio

$\alpha_{i,HK}$ – Relative volatility between i and the heavy component

θ – Relative volatility between light component and the heavy component

For this study, Aspen Plus recommended an initial value of 1.5. In fractional condensation, the temperature and the pressure of the flash drum are specified by the user.

The phenol recovery model comprises of a heaters, a pre-flash column, flash drum and the fractionation column. As can be seen in Figure 17, bio-oil vapours first enter the fractional condensation unit, where phenols condense out from water at the optimum

condensation temperature. The concentrated phenolic solution then passes onto the Pre-Flash column where water and the highly volatile phenols undergo partial vaporization. The feed stream enters the pre-flash tower at stage 22 via the furnace, numbered from the bottom up. Operating pressure in the column is 1 bar and the temperature is 100°C–180°C. The concentrated phenolic mixture stream (PHNOLICS) is fed into fractionation column (FRACT) as shown in Figure 17, where it enters in stage 23, numbered from the bottom up. The PHNOLICS stream is upgraded in a 20-tray splitting column, to give phenolic fractions consisting of syringol, guaiacol, syringaldehyde, and cresol as per the purities shown in Table 5. The bottoms from the fractionation column exits at 270 - 300◦C as creosote that is composed of heavy phenolic compounds such oligomers. The pre-flash column has a condenser and decanter to enable separation of the condensed volatile phenols from water. From the boiling points of the phenols in lignin bio-oil, it was noted that the three phenols that will be entrapped with the water during partial vaporization are phenol, p-cresol and o-cresol. The phenol mixture (i.e. stream PHNOLICS) now composed of phenols of low volatility are then sent to the fractionation column FRACT, where they are fractionated according to the product specification shown Table 5.

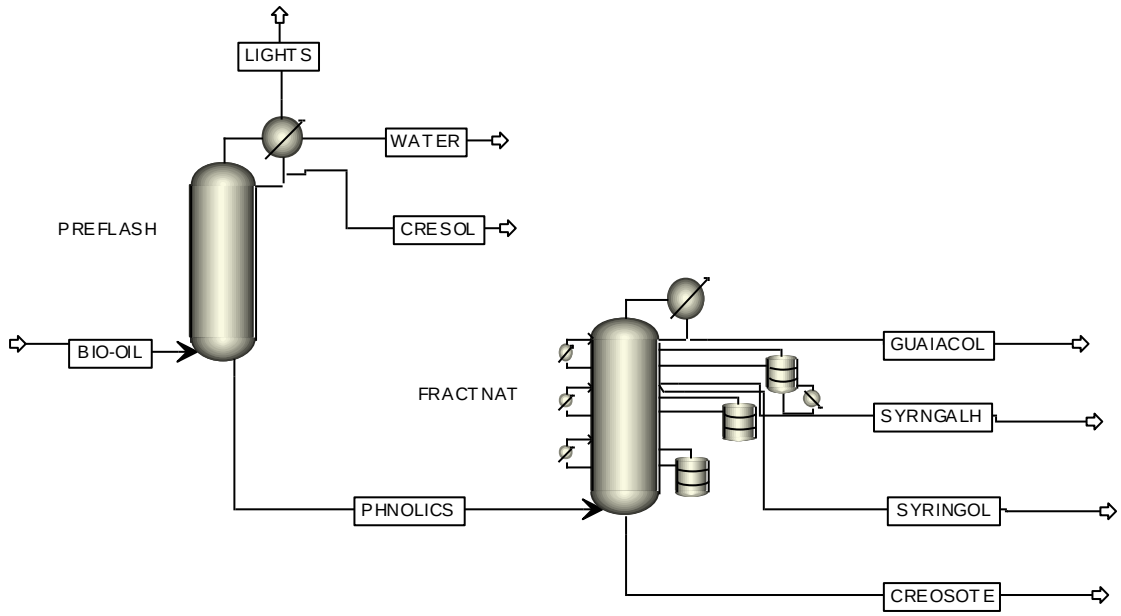


Figure 17 Aspen Plus® Bio-oil Fractionation Model

Since short methods such as equations 4 and 5 are embedded in Aspen Plus® Fortran modules, the Aspen Plus® design specification tool was used to determine optimum values of parameters such as reflux ratio and the number of plates, based on distillate flow rate, minimum number of plates, reboiler duty and minimum reflux ratio, so as to meet the product specifications of the phenolic fractions shown in Table 5. Since price of the column increases with pressure, it was decided to use atmospheric pressure (i.e. 1 Bar) so as to reduce capital costs.

The followings are assumptions made for fractional distillation simulation based on the fractional distillation simulation studies of Ne et al [39], Ralph et al [176].

i. There is no heat loss from columns to the surroundings
ii. The energy to the column is supplied in the form of steam
iii. Cooling water is used to cool the components in the condenser
iv. Interfacial resistance is negligible
v. Mixing of components is uniform within the whole column

All the units and tools discussed above enable Aspen Plus® to predict the mass and energy balance but accuracy of the prediction is dependent on the selected thermodynamic method.

3.3.1 Selection of thermodynamic model

Selection of thermodynamic properties for design calculations is a very important as it enables an accurate description of the system which is being modelled [177]. Application of the inappropriate property methods results in inaccurate mass and energy balances which in turn has a drastic impact on the cost and safety impacts on the designed plant. Several property models have been developed over time but can generally be grouped into activity coefficient models and equation of state models[139][178].

Physical property methods used in Aspen Plus® for simulation calculations are either based on a property model or on a grouping of these property models [164]. Simple methods, for instance, use the ideal models whilst advanced methods are a

combination of equation of state and activity coefficient models. In a combined property method the vapour phase calculations can be done using an equation of state model, and the liquid phase done using an activity coefficient method [56][177].

In order to select a property method properly, the system in question needs to be defined in terms of its components before application of any algorithms can be done. The nature of the components and the level of their interaction determine which equation of state applies in that particular case [179]. There are several methods of selecting property methods in literature but in the current work only the Aspen method was reviewed.

The Aspen Plus® algorithm begins by first determining if there are polar conditions in the system [141]. If not present the equation of state is chosen but if the polar conditions exists, critical operating conditions are used to determine if the activity coefficient based method can be used with the Henry Law or on its own [178]. Based on this algorithm, the appropriate thermodynamic method for this study was determined to be UNIQUAC. Since data on ternary and multi component system is unavailable for pyrolysis oil compounds, verification of the thermodynamic method is done by comparing the predictions of the thermodynamic model to pyrolysis reactor experimental data specifically the yields of bio-oil compounds.

3.4 Simulation and convergence

Aspen Plus® operations are based on iterative processes that require the equations to converge so as to determine the solution for mathematical models. If there are any errors such as data specification such as for operating parameter, the process will not converge, the process development will need to be checked again. If the process converges, the model is validated using experimental data or literature data.

3.5 Validation of models

Validation of models is necessary part of the process as it enables any uncertainty about the model capabilities to be identified, so as to produce an accurate and credible model. The process begins with validation of the thermodynamic method as it is crucial

in producing a product distribution that fits well with experimental data. For this study validation of the chosen thermodynamic method (i.e. UNIQAUC) was performed by first substantiating the accuracy of the input parameters such as binary parameters for the components such as the phenolic compounds, water, char, etc. There after the property method was used to generate critical values of critical parameters; these values were then compared with experimental data of similar mixtures. If the variation between the thermodynamic model prediction and experimental data is within the 95% confidence interval, then the model was deemed valid, but if it bigger than this margin, then another thermodynamic model would be chosen. But since lignin based bio-oil is composed of a multiple of phenolic compounds of which the VLE diagrams are not available in literature, validation was performed by comparing the VLE of targeted phenolic fractions with experimental data.

Statistical Tools such as ANOVA are used to determine the variation between the model predictions and the literature reported data. The confidence interval and hypothesis test are used to determine the accuracy and validity of the model. In the case of the study, the results of the catalytic lignin pyrolysis reactor were compared to the literature data and thereafter the variation between the model results (such as yields of char, phenolic compounds, and non-condensable gases) and literature were determined. The validation for the reactor model had two parts, as per the two parts in the model, where by the first part predicts the products spectra of non-catalytic pyrolysis (i.e. Block PYROLYSI in the Aspen Plus® reactor model) and second part predicts the products of catalytic pyrolysis (i.e. Block CATALYSI in the Aspen Plus® reactor block) using input from the product spectra of non-catalytic pyrolysis. Since Aspen Plus®models involved use of two different catalysts, validation of the catalytic pyrolysis product spectra had two scenarios. The confidence interval indicated credibility of the model. Since pyrolysis has multiple reaction pathways, it would require a flexible thermodynamic model that would be able to describe simultaneously polar, associating and polymeric compounds as well as gaseous compounds. But this will further require more extensive multi-component equilibrium measurements.

Since such measurements are not available in literature, validation of the catalytic pyrolysis section of the reactor model was done by comparing the weight percentage fractions of phenolic compounds with experimental data of catalytic pyrolysis of lignin. In the case of the phenol fractionation model, the compositions of the phenolic fraction were compared to the targeted phenolic fractions found on the phenol market.

The utility requirements for the model were sourced from the sugarcane biorefinery as per specification of the Aspen Plus® Utility Tool.

3.6 Process analysis

This step involves assessment of the results of the simulation so as to identify the trends in the process to meet specific objectives. In this study four scenarios for producing phenolic compounds from lignin were developed and thereafter based on the mass and energy balances, the trends of process variables such yield, condenser phenolic yield were assessed.

In the field of pyrolysis of lignin, optimum pyrolysis vapour condensation temperature for production of concentrated phenol rich bio-oil is parameter that is hardly reported as it requires a lot of experimental data such as heat loss, losses in components during condensation, yields of phenolic condensate, temperature, capital cost, cost of lost desired product and operating costing etc.. Thus this phenomenon was explored in this study as Aspen Plus® has all the necessary tools to make this possible, such as the Activate Economics tool. Also by running simulations using these optimum temperatures, energy integration of the pyrolysis process could be performed, to determine where the energy savings around the pyrolysis reactor. In order to optimise the condenser temperature, data on parameters such as heat loss, phenolic losses, phenolic content in bio-oil and water content in bio-oil is required. These parameters were deduced by running several simulations within the condenser temperature range of 25 – 100^{o}C. This temperature range was chosen based on the dew point of water as it is below the phenolic boiling temperature range of 180 – 240^{o}C.

Also since temperature has significant effect on the phenolic fraction produced during fractionation of the crude phenolic mixture thus column perform enables the temperature and pressure of the fraction column to be optimised.

3.7 Economic analysis

When a chemical plant such as a lignin pyrolysis plant is constructed, the investment costs need to be first determined such as the capital expenditure (CAPEX), operating expenditure (OPEX), and there after an economic evaluation is performed. The process of economic evaluation of a plant first begins with the preparation of process flowsheet diagrams that show several routes of producing the desired products. Thereafter models are developed in simulation software such as Aspen Plus® based on the process flowsheet diagrams. Based on the operating conditions, mass and energy balances are thereafter developed using Aspen Plus®. Using these mass and energy balances, the Aspen Plus® performs the sizing and costing of the equipment thus enabling the economic valuation to be performed. The economic feasibility of the plant is thereafter determined by either evaluating the internal rate of return on the investment (IRR) or by determining the product's minimum selling prices (MSPs). If the route of determining the IRR is chosen, the market selling prices are used. Since CAPEX is usually sourced from investors that expect returns on their investments, the IRR needs to be above the minimum IRR. If the route of minimum selling price is chosen, the IRR is first set the minimum acceptable market value and thereafter the selling price is manipulated to achieve this set IRR. This selling price is known as minimum selling price.

3.7.1 Capital Expenditure

The generated mass and energy balances are imported into the Aspen Process Economic Analyser tool so as to determine the capital cost associated with each standard process unit. Non-standard equipment such as the pyrolysis reactor are estimated using sizing methods outlined in the Fogler et al [141]. Other costs associated with capital cost such as working capital, insurance, installation and taxation are incorporated as percentages of the fixed capital expenditure. For the case of this study, the chemical engineering plant cost indices were used for determining the equipment costs of non-standard equipment such as the pyrolysis reactors. Sizing of the reactor was based on a similar fast pyrolysis unit of National Renewable Energy Laboratory (NREL) which was covered in the studies by Wright et al [2]. Since the size of any equipment is known to change linearly with the inlet flow, this assumption was used as basis for sizing the reactor. As this report by covers Wright et al [2] fast pyrolysis of biomass, it was assumed the residence time would be the same as that of this study. This was based on the fact that pyrolysis is a complex process with various reaction pathways at any specific temperature thus the residence lie within specific range instead of having a specific value.

3.7.2 Operating Expenditure

Operating costs incorporate all the expenses associated with running and maintaining the process. These costs fall under two categories namely fixed operating cost and variable costs. Variable operating costs change with time over the running of the process and they are namely cost of raw materials, energy, waste treatment, utilities and chemicals. In the case of this study, cost of utilities and energy are determined from the mass and energy balances developed in simulation models such as Aspen Plus®.

The price of lignin feedstock was estimated based on the unit price of coal and heating value of coal.

$$Cost\ of\ lignin = \frac{(Heating\ Value\ of\ Lignin)x(Cost\ of\ coal)}{Heating\ value\ of\ coal}$$

Equation 6

The averaged South African coal export price is based on the financial period 2015 [180]. Cost of catalysts were based on market values. Fixed operating costs are expenses associated with the operation that do not change during operation and they must be paid regardless of the capacity performance of the plant. These costs are namely salaries, rent, insurance, security etc. For this study, insurance, rent were defined as percentages of inside battery limit.

3.7.3 Economic indicators

Depending on the method chosen for economic feasibility, be it either via determining the internal return on investment (IRR) or determining the minimum selling price (MSP), the economic indicator will need to meet the minimum acceptable value. Since models in this study have multiple products, economic analysis based on the minimum selling price is not feasible due to the complexities associated with manipulation of the selling price during economic evaluation. Thus it was decided to perform the economic analysis by determining the IRR based on the market prices of the phenolic fractions. Also due to the unavailability of historical price trends of phenolic fractions, it was decided to perform the cash flow analysis based on real terms.

In order to determine the effect of different parameters on the economic, sensitivity analysis is applied. Sensitivity analysis determines the effect of an uncertainty on the costs of a model. Sensitivity analysis enables identification of dependent and independent variables that have a major effect on the optimum operation of a process. Thus this enables decisions about the process to be taken with confidence as the consequences of the change of every variable will be known. The economic model was developed using Microsoft Excel based on the economic assumptions in Table 11, the mass and energy balances from the Aspen Plus® models and the CAPEX and OPEX of the Aspen Plus® models.

Table 11 Economic assumptions for the development of the techno-economic analysis [2][51]

Parameters	Value
Annual operating hours (9 months)	6480 h
Equity: loan	40%: 60%
Loan interest	10.5%
Loan term years	10
Working capital (% of FCI)	5.00%
Depreciation period (years)	25
Salvage value	0
Depreciation method	Straight line
Construction period (years)	2
% Spent in year -2	10%
% Spent in year -1	60%
% Spent in year 0	30%
Start-up duration (years)	2
First year capacity (% design)	50%
Second year capacity (% design)	75%
Income Tax Rate	28.00%
Cost Year for Analysis	2015
Inflation Rate	5.70%
Minimum acceptable %IRR (real term)	9.70%
Minimum acceptable %IRR (nominal term)	15%
Currency conversion US $ 1 =	14 ZAR
Phenol price (purity 99.5%) (US $/litre)	US$1500 [a]
Sugarcane bagasse price (US $/ton)	0 [b]
Sugarcane trash price (US $/ton)	(28.24+25.71)=53.95 [c]
Coal price (US $/ton)	57.04 [d]
Phenolic fraction Price[f]	
Cresol fraction (US$ per ton)	3000
Syringol fraction (US$ per ton)	6000
Syringaldehyde fraction (US$ per ton)	6000
Guaiacol fraction (US$ per ton)	6000
Creosote (US$ per ton)	650

[a:] From http://www.platts.com

[b:] The thermal and electrical power required for the lignin pyrolysis plant is supplied by CHP unit of the integrated bio-refinery

[c:] The price of brown leaves (trash) was estimated based on the unit price of coal and heating value of trash in proportion to coal plus the collection cost (Smithers et al)

$$Cost\ of\ lignin = (Heating\ Value\ of\ Lignin)x(Cost\ of\ coal)/(Heating\ Value\ of\ Coal) \qquad Equation\ 7$$

[d:] The averaged South African coal export price for 2015 from (www.indexmundi.com)

* Based on NED bank and Standard Bank Loan interest rate

[f] Market price is the average market price based on the price ranges in Table 5.

3.8 Environmental Impact analysis

During sugarcane farming, transportation is required for transfer of utilities from suppliers to farm and also for delivering the harvested sugar cane to the mill. Each phase of this supply chain is associated with a certain amount of Green House Gas emissions (GHG)[181]. Also the bagasse itself that is produced as waste produced after sugar extraction is associated with a certain amount of GHG. Since this study is investigates on the lignin based phenols, the base case of this study is the CO_2 emissions associated with fossil based phenols.

Currently the majority of the phenols in the market are from fossil based sources. Thus by comparing the CO_2 emissions of the developed model to the CO_2 emissions of fossil based sources, the impact of the developed models can be determined [181][73]. For this study the system boundary begins at the lignin residue stream from the biochemical sugarcane-lignocellulose biorefinery and ends at the conversion of lignin into phenol.

GHG emissions are determined by employing the emission factors associated with each gas emitted to the atmosphere (i.e. CH_4, NO_2, CO_2,) so as to determine the total carbon dioxide equivalent (CO_2.e). The CO_2.e is used to determine the Global Warming Potential (GWP) which is the total heat the CO_2 gas traps into the atmosphere. In the case of this project the char and the pyro gas is combusted where only CO_2 is released into the atmosphere.

CHAPTER 4

RESULTS and DISCUSSION

The results of the various process simulations are presented as process analysis and economic analysis below. The process analysis discusses the validation of the thermodynamic method and Aspen Plus® model, optimisation of pyrolysis parameters and environmental CO_2 emissions. Results of the economic analysis delves into the economic parameters and indicators for the developed scenarios.

4.1 Process Analysis

4.1.1 Validation of thermodynamic method

Table 12 shows the comparison of prediction of critical parameters the UNIQUAC method with the works of Xianjun et al [182],Faravelli et al [104] and Olga et al[158].

Table 12 Comparison of predictions of critical parameters and lignin density of UNIQAUC method with experimental data (Olga et al. [153]).

	Phenolic compound parameters		**Lignin parameters**	
	Critical Temperature, T_c (°C)	Critical Pressure, P_c (Bar)	Density, ρ (kg/m^3)	Lower heating value (MJ/kg)
Model	1290	47	1239	20.8
Literature data	1320	45	1291	21.3

Model predictions for the critical temperature and pressure for the phenolic compounds produced average variation of 2.27% and 4.44 % respectively. As for the parameters of lignin, the model produced average variation of 6.84% and 2.34% for density and lower heating value respectively. It can be seen that the model thermodynamic method predictions correlate well with experimental data reported by the works of Olga et al [158], whom reported similar values for the variations based on various thermodynamic methods. The UNIQAUC thermodynamic method was thus deemed valid for predicting the product spectra of the lignin pyrolysis model.

4.1.2 Validation of the Aspen Plus® models

Since the validation Aspen Plus® pyrolysis reactor model is composed of two parts as mentioned in the section *3.5 Validation of models*, the first validation to be discussed is for non-catalytic pyrolysis of lignin. Figure 18 shows a comparison of model results of non-catalytic pyrolysis of lignin with experimental data of Shen et al [183] and Trinh et al [116].

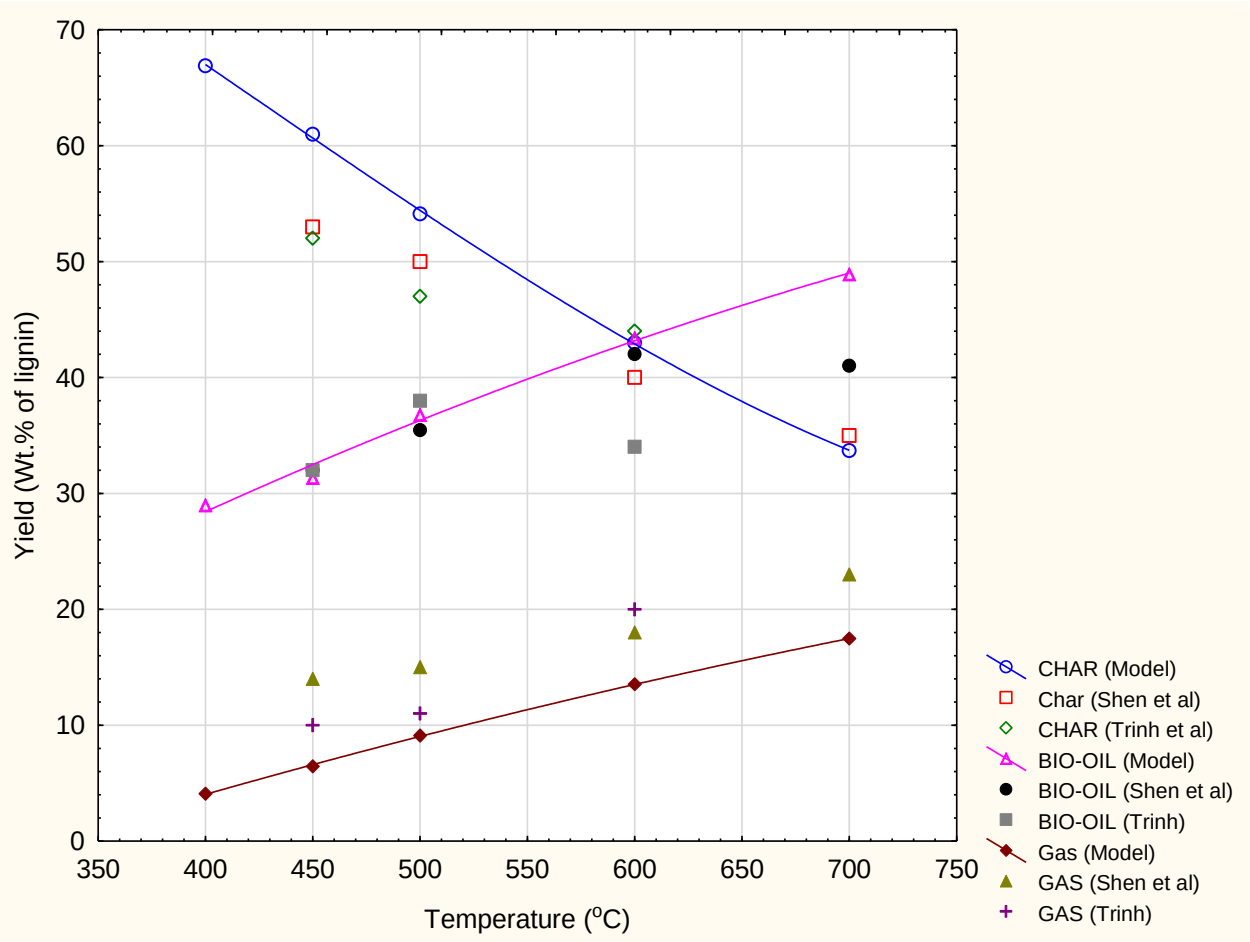


Figure 18 Comparison of Char Yields of Model to Organics yields of Experimental data

It can be seen from Figure 18 that the pyrolysis reaction model results correlate well with experimental data, particularly between 400°C and 800°C for the gas yields. This was attributed to the relatively high yields of gases CO, CO_2 and CH_4 in the gas stream. The relative error of the model prediction small (Relative error < 3%). This in turn made the predictions of gas yields correlate well with experimental data. The model predictions were found to correlate experimental for char yields throughout the

temperature range of 400 – 800°C as seen in Figure 19. This reciprocal relation between the model and experimental data was mainly due to the high carbon content in lignin derived bio char (i.e. carbon content >98 wt.% [91][92]).

Correlation between the model and experimental data was found to be unsatisfactory for bio-oil yields results within the range 400 - 500°C. At higher temperatures within the range 500 - 800°C, the model results were in agreement with experimental data.

Based on this statistical analysis above, the model was deemed valid for the temperature range 500 – 800°C and thus could be confidently used for process and economic analysis for pyrolysis optimum temperatures within this range.

Table 13 shows the comparison of yields of non-catalytic lignin product, as predicted by process simulations, in comparison with the works of Lou et al [91], Peng et al[56], and Trinh et al[92]. It can be seen that the model results correlated better for char and gaseous products, as the predicted yields were within range of reported experimental data. This is in agreement with the trend depicted in Figure 18. The model under predicts the yields of oligomers as evidenced by the range of the model that is has a minimum oligomer yield of 14 wt.% of lignin compared to the minimum oligomer experimental yield of 19 wt.% of lignin. The experimental oligomer maximum yield was found to be greater than the model oligomer yield by 4 wt.% of lignin. This observation was mainly due to the unavailability of detailed data that shows characterisation of lignin oligomer in bio-oil. In addition, data on secondary tar cracking reactions in the bio-oil that describe tar products was not available. It was reported that the phenols tend to re-isomerise into large lignin monomers during pyrolysis of lignin thus causing variations in the yields of oligomers [43].

Table 13 Comparison of Model Phenolic compounds yields to experimental data (within the range pyrolysis temperature 400 - 800°C)

Component	Model wt.% Lignin	Experimental data wt.% lignin
Water	2.67 – 9.86	3.23 – 10.78
Char	28 – 32	25 – 45
Carbon monoxide	1.90 - 9.12	1.78 – 8.87
Carbon dioxide	4.56 - 6.78	5.67 - 9.76
Methane	2.98 - 5.23	3.12 - 4.94
Phenolic compounds		
Phenol	0.05 - 0.90	0.01 - 0.98
P-cresol	0.03 - 0.52	0.01 - 0.45
Methoxy-phenol	0.02 - 0.05	0.01 - 0.08
Vanillin	0.12 - 0.31	0.10 - 0.35
O-cresol	0.04 - 0.29	0.01 - 0.36
Catechol	0.03 - 0.65	0.04 - 0.69
Vinyl Guaiacol	0.8 - 1.65	0.78 - 1.98
Guaiacol	0.31 - 0.83	0.25 - 0.92
Eugenol	0.21 - 0.28	0.19 - 0.31
Syringol	0.42 - 1.51	0.46 - 1.65
Acetosyringone	0.12 - 0.16	0.13 - 0.23
Methyl-1,2-benzenetriol	0.31 - 1.12	0.21 - 1.34
Syringaldehyde	0.56 - 0.89	0.51 - 0.98
Acetovanillone	0.11 - 0.15	0.09 - 0.19
Xylenol	0.10 - 0.15	0.098 - 0.18
Oligomers	14- 23	19 – 24

In this study oligomers are not in this list of targeted phenolic products, thus this variation between the model oligomers yields and reported data does not affect the integrity of the model. Since the yields of targeted phenolic compounds were found to correlate with experimental data and oligomers. Also since the model, was found to correlate with reported data, the model was declared valid for predicting the product spectra of non-catalytic pyrolysis. As mentioned in section *3.5 Validation of models*, validation of the lignin catalytic pyrolysis section of the Aspen Plus® model is in two parts (i.e. for NaOH catalyst based process and the Zeolite catalyst based process).

For zeolite catalyst based lignin pyrolysis process, validation was performed by comparing the model results to the works of Mullen et al [24] as shown by the comparisons in Figure 19 and Figure 20. Due to the limitation of articles that used

reported catalytic pyrolysis yield results of non-woody biomass using zeolite catalyst, the comparison of model results to experimental was limited to one article.

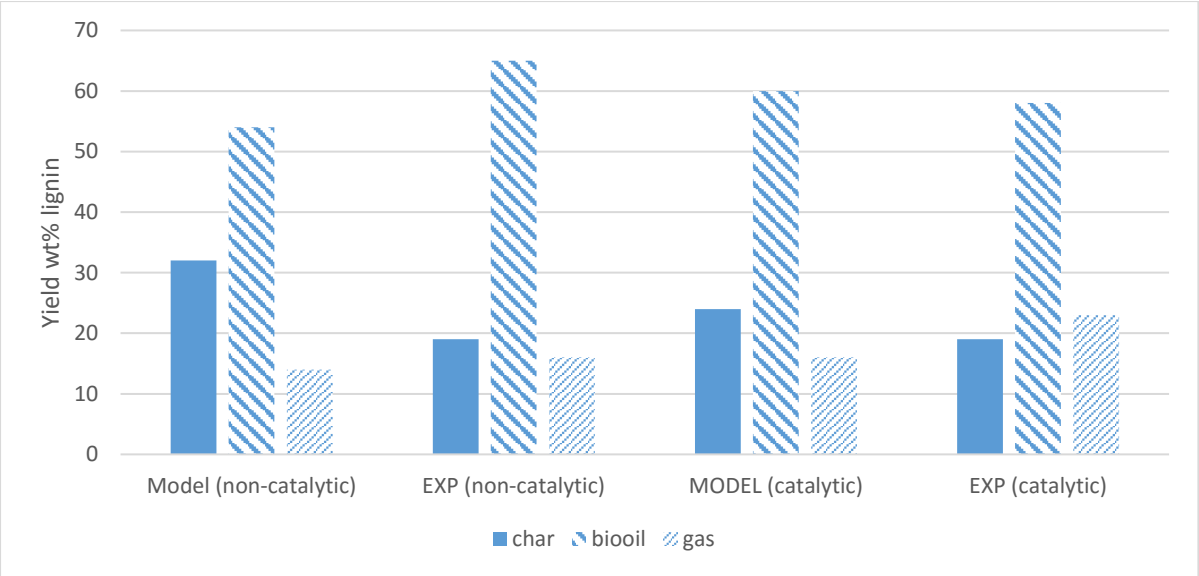


Figure 19 Influence of Zeolite catalyst on pyrolysis yields on the model and experimental results from Mullen et al [24] *at 550°C*

Comparison of non-catalytic results for the model to experimental data shows that the model over predicted the yields of char and under predicted the yields of gases. The main reason for this difference is that the model uses results from articles that uses lignin from different non-woody biomass, whilst Mullen et al [24] used only Asian and bagasse lignin from non woody biomass. Since the comparison was limited to one article, the difference in feed composition between the model predictions and experimental data had significant effect on the variation of yields for the pyrolysis products.

Comparison of the model non-catalytic yields and the model catalytic yields, showed that the bio-oil yield increased by 5 wt. % of lignin whilst the comparison experimental non-catalytic and catalytic yields of the bio-oil showed a decrease of 4.5 wt. % of lignin. But comparison of bio-oil yields for catalytic pyrolysis of the model were found to correlate well with experimental data. This was mainly due to the fact that at the optimum pyrolysis temperature of 550°C (i.e. temperature with maximum yield of biooil) which was used by Mullen et al [24] and in the model, the effects of re-

isomerisation of oligomers is not significant as compared to other temperatures with lower yields [149][169].

For the model, the char yields decreased by 6 wt.% of lignin, when the conditions changed from non-catalytic to catalytic conditions. This was attributed to the conversion of oligomers with high molecular weight (mainly entrapped onto the char) into phenolic compounds of lower molecular weight, thus lowering the char yield. Under catalytic conditions, the model yields correlated well with experimental data as seen in Figure 19.

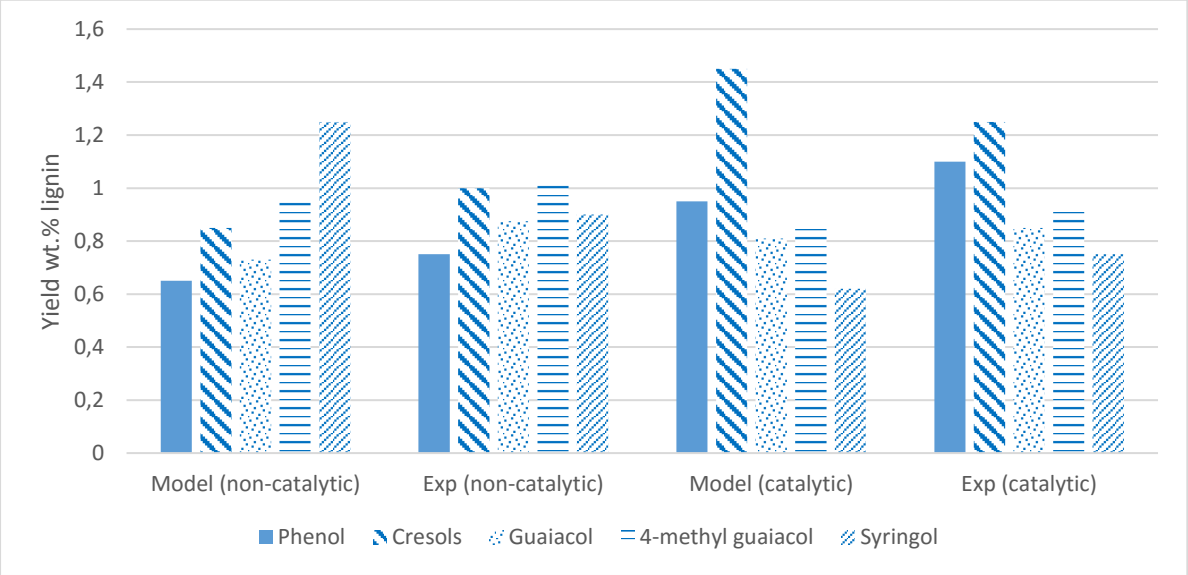


Figure 20 Influence of Zeolite catalyst on phenolic yields on the model and experimental results from Mullen et al [24] *at 550°C*

Predictions for the gas yields for the model increased in accordance with experimental data when conditions changed from non-catalytic to catalytic conditions. But the model gas yield and experimental data differed by 4%Wt. lignin. The variation is between the model and experimental gas yields is attributed to the limitation of the model in using yield data of only three gases (i.e. CO, CH_4, CO_2) whilst in the experimental gas yield, all gases are accounted for. In order to demonstrate how the model preforms in predicting individual phenolic compounds, model predictions were compared with experimental data as shown in Figure 20. Mullen et al [24] reported

only five phenolic compounds thus comparison of model with experimental data was limited to these specific phenolic compounds.

Deviations of the model predictions from the experiments were less noticeable for low boiling point phenolic compounds such as phenol, o-cresol and p-cresol. By comparing the non-catalytic conditions and catalytic conditions for the model, it can be seen that yields of these low boiling phenolic compounds increased by 0.28, 0.61 and 0.1 wt.% lignin for phenol, cresols and guaiacol respectively. This was in agreement with the increases for the experimental data where phenol, cresols and guaiacol increased by 0.18, 0.64 and 0.01 wt.% lignin. Model yields for methyl guaiacol and syringol decreased by 0.1 and 0.24 wt.% lignin respectively. The decrease in yields was due to their conversion into low boiling point phenolic compounds, such as phenol and cresol, via cracking of methoxyl groups and phenolic hydroxyl groups on benzene unit. This was in agreement with the observations of Mullen et al [24], where it was reported these two phenolic compounds decreased by close margins of 0.5 and 0.6 wt.% lignin for methyl guaiacol and syringol respectively. For the NaOH based pyrolysis process, validation of the lignin pyrolysis catalytic section of the Aspen Plus® model was performed by comparing the bio-oil composition of the model to the works of Peng et al [56] as illustrated in the comparison in Figure 21.

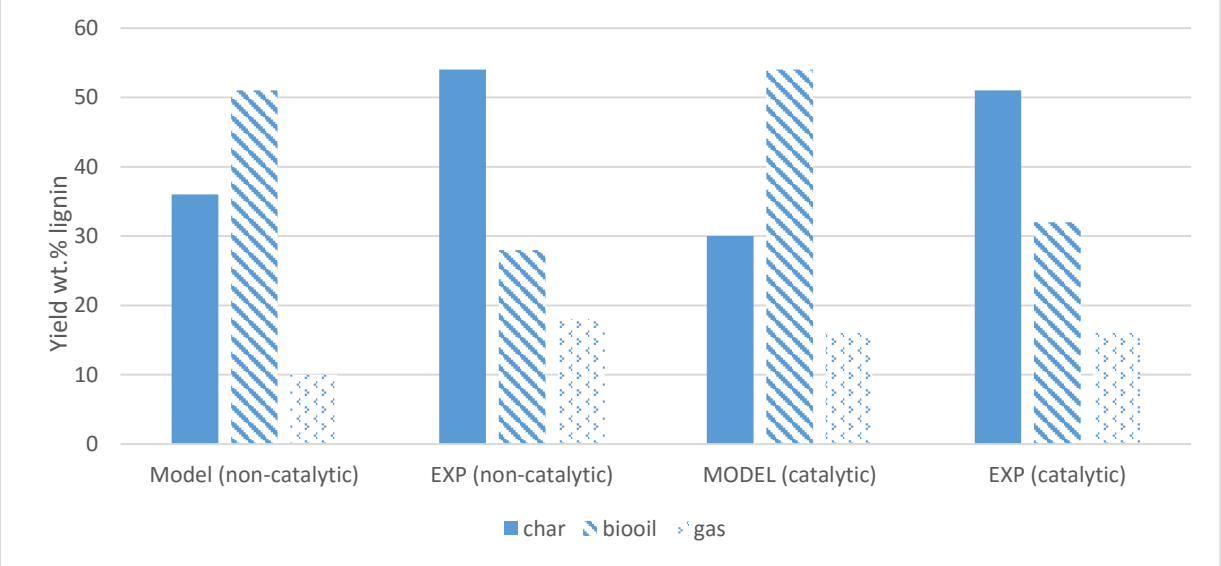


Figure 21 Influence of Sodium Hydroxide catalyst on pyrolysis yields on the model and experimental results from Peng et al [56] at 450°C

Comparison of non-catalytic model predictions with non-catalytic experimental data shows a marginal difference in yields of bio-oil, char and gases. This was expected due to unavailability of a broad database for catalytic pyrolysis of lignin using alkaline catalysts, which limited the comparison of model results with article in literature. Validation using one article limits the data range that can used for validation since using various articles limits the effects of changes in mean and variance of the distribution. Thus the validation of model via comparison with experimental data is now a probabilistic based process. When the conditions changed from non-catalytic to catalytic, it can be seen the model predictions correlated well with experimental data in terms of changes in yields of char, and bio-oil. As can be seen from Figure 21, for the model, char and bio-oil yields changed by 5 and 4 wt.% lignin, respectively, whilst for the experimental data the changes for char and bio-oil was 3 and 4 wt.% lignin. This observation validated the kinetics the Aspen Plus® lignin catalytic pyrolysis model.

Validation of the model prediction of phenolic distribution could not be performed by comparison of the yields of phenolic yields of phenolic compounds due to the fact that the experimental phenolic distribution data was expressed in percentage area. But it was noted that a qualitative comparison could be performed based on the yield evolution of phenolic compounds when the conditions changed from non-catalytic to catalytic as shown in Figure 23.

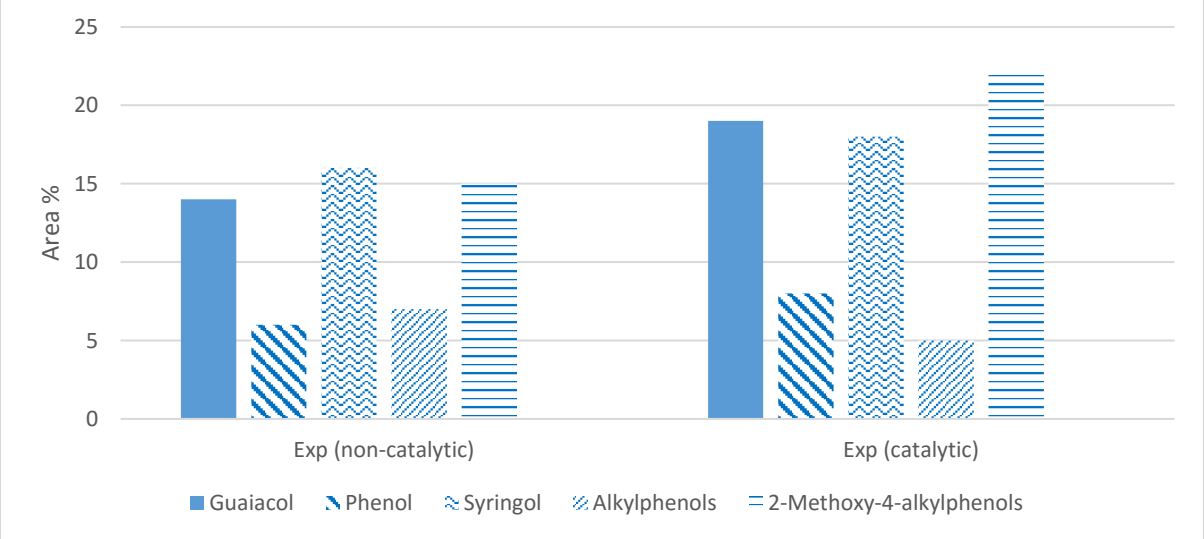


Figure 22 (a) Influence of Sodium Hydroxide catalyst on pyrolysis yields of lignin pyrolysis results of Peng et al [56]) at 450°C

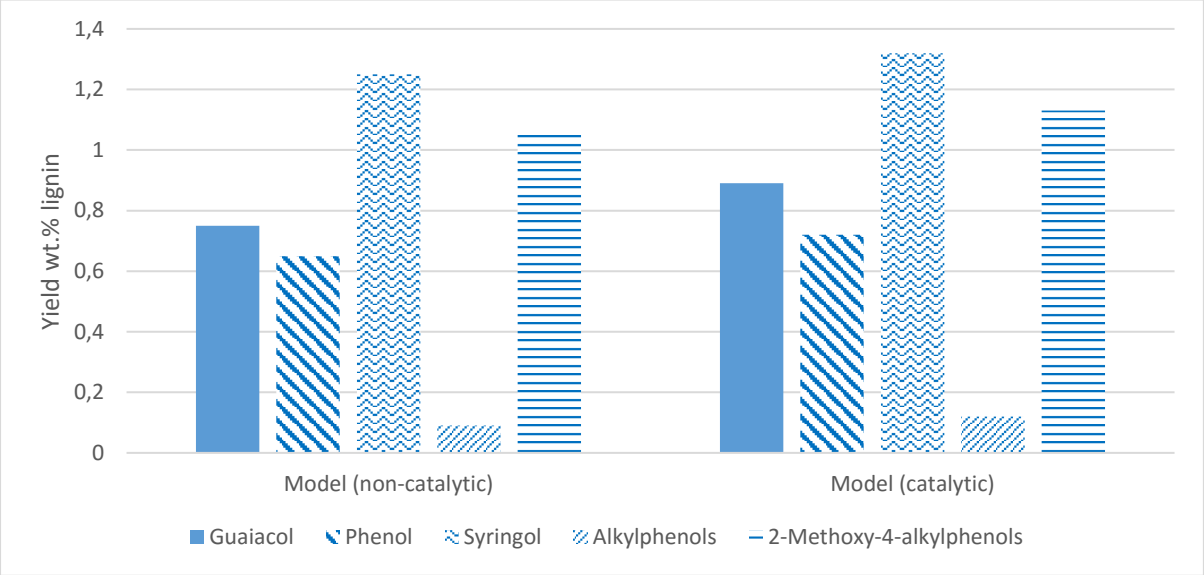


Figure 23 (b) Influence of Sodium Hydroxide catalyst on pyrolysis yields of the model at 450°C

The model prediction had an increase of 5, 3, and 3 % for guaiacol, phenol and syringol respectively, whilst the experimental data reported an increase of 5, 3, and 4 % for guaiacol, phenol and syringol respectively. Since these increases for both the model and experimental data are relatively similar, the model was found to correlate well with experimental data when predicting increases for low molecular weight phenolic compounds such as phenol. Deviations of the model predictions from the experiment data were more noticeable for high boiling compounds, as evidenced by the prediction for the 2-methoxy-alkylphenols compounds. This evident from the observation of Figure 23 where experimental data reported a 14 % increase whilst the model showed a change of 3 %. Since the units are not the same, a qualitative approach shows that the model under predicts the yields of large molecular weight phenolic compounds. This mainly due to the unavailability of kinetic data for catalytic cracking of the functional methoxy groups attached onto benzene unit into mono-phenol.

Although there were variations between experimental data and the model predictions, the difference was found not to be significant to affect the accuracy of the model in predicting non-catalytic and catalytic pyrolysis product distributions, the model was deemed valid based on the above mentioned observations. This also affirms that the assumptions made about the model are valid.

Since the phenolic mixture is fractionated, validation of the fractionator is shown in Table 14.

Table 14 Comparison of model and literature data

Phenolic fraction	Model prediction		Literature data [16][95][13][146]	
	Composition (wt.% mass)	Temperature	Composition (wt.% mass)	Temperature
Cresol	0.453	200	0.434	213
Guaiacol	0.498	210	0.478	218
Syringol	0.634	231	0.603	234
Syringalhyde	0.431	235	0.412	243

Table 14 shows that the maximum deviation between the model prediction and literature data at the top distillate is 8.33% (i.e. the cresol fraction). Deviations between the model and literature data for middle fractions was 6.06%, 4.92% and 4.61% for guaiacol, syringol and syringalhyde fraction respectively. Thus it can be seen from the variations that the model can be confidently used to perform process and economic analysis.

4.1.3 Process analysis of the lignin pyrolysis reactor

The mass and energy balances for the investigated processes resulted from the Aspen Plus simulations, is summarized in Table 15 .

Table 15 Summary of mass and energy balances

Parameter	Unit	Scenario 1	Scenario 2
Feedstock to lignin bio-refinery	kg/hr	5525	5525
Optimum pyrolysis temperature	^{o}C	450	550
Catalyst consumption	kg/hr	1105	1
Products			
Char	kg/hr	1658	1602
Gases	kg/hr	1105	1048
Cresol Flowrate	kg/hr	-	-
Syringaldehyde fraction flowrate	kg/hr	-	-
Guaiacol fraction flowrate	kg/hr	-	-
Syringol fraction flowrate	kg/hr	-	-
Creosote	kg/hr	2763	2873
Energy Demands			
Cooling demand	MW	4	4.2
Heating demand	MW	4.1	4.3

As can be seen from the detailed mass ad energy balances in the Table 15, in all scenarios the majority of the phenolic compounds had individual yields of less than 1 wt. % of lignin on a dry-ash-free basis. Char yields for scenario 1 was 34 wt.% of lignin, whilst for scenario 2, the char yields was 31 Wt.% of lignin. This is in agreement with the reported char yields Peng et al [24] and De Wild et al [151]. Non-condensable gas yields show that the yields were 4 Wt. % of lignin higher in scenario 1 compared to scenario 2 and this was mainly due to use of different catalysts. In terms of energy demands, the cooling demands was 4.0 and 4.2 MW for scenario 1 and 2 respectively. The differences in cooling demands between these scenarios were mainly due to the difference in enthalpy of the pyrolysis products that was attributed to the difference in pyrolysis temperature where scenario 1 operated at 450^{o}C whilst scenario 2 operated at 550^{o}C.

Since in scenario 1, the process was optimised so that it is self-energy sufficient and also simultaneously produce residual char that can be sold to generate revenue, it was found necessary to perform heat integration of scenario 2 where excess energy was produced. The heat integration enables reduction in utility demands, thus heat integration of scenario 2 showed that the energy produced from burning the char was enough to preheat the feed (i.e. lignin) and also supply heat energy to the pyrolysis reactor. This resulted in excess energy of energy 2.4MW exiting the pyrolysis plant. Therefore the lignin heater (XHI in Figure 24) can be used for start-up operations and when the process is steady state, the heat from the combustor can be used to pre-heat the lignin and meet the reactor energy demands. .

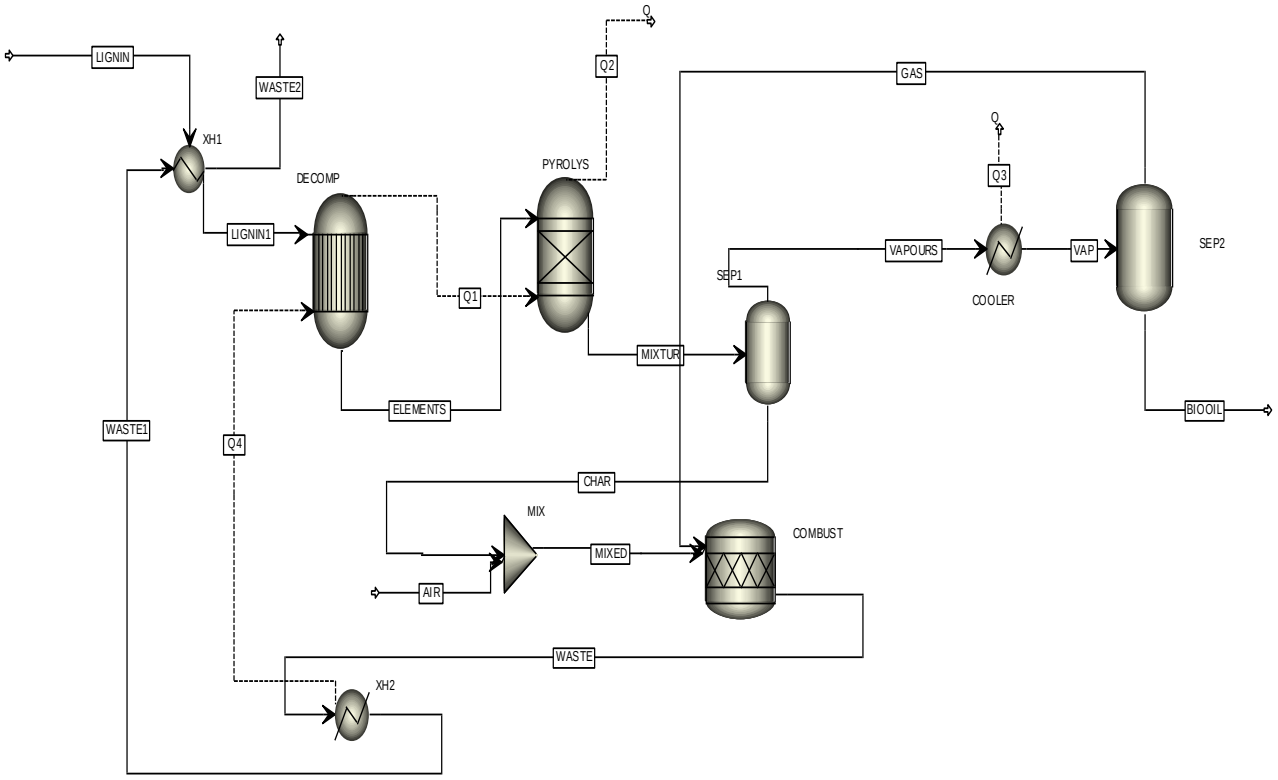


Figure 24 Energy Integration of the lignin pyrolysis model

4.1.3.1 Optimisation of the pyrolysis reactor condenser temperature for production of creosote

Since the parameters that affect fast pyrolysis of lignin have been accounted for, in the literature survey, the optimum temperature was 450^{o}C and 550^{o}C for scenario 1 and 2 respectively, the mass flow rates of the vapours and non-condensable gases were used determine the optimum condenser temperature for the fractional condensation unit.

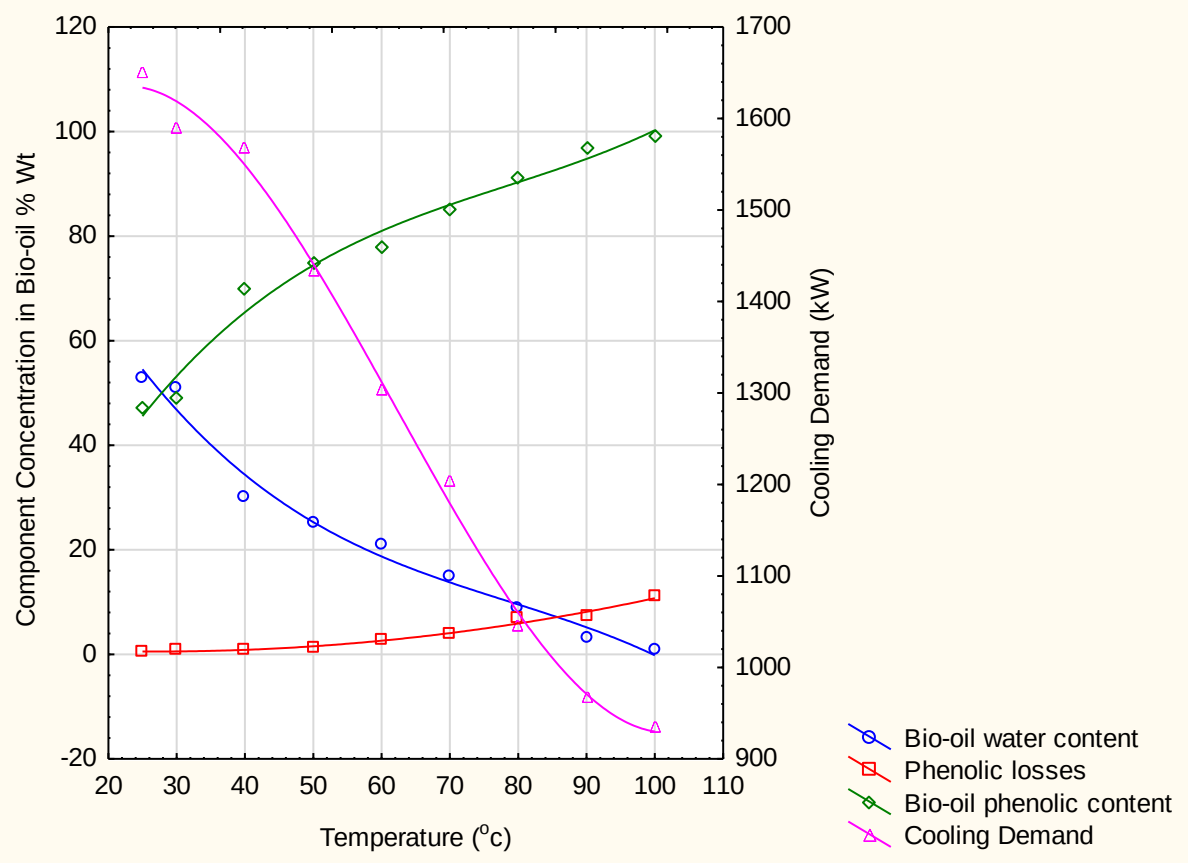


Figure 25 Variation of several parameters with condenser temperature for Scenario 1

For scenario 2 the variation is shown in Figure 26. It was noted that as the temperature increased from 25 to 100°C, the phenolic losses increased from 1.2 to 12% of the total bio-oil mass. This was the same observation in scenario 1, but the difference is that the losses of scenario 2 were less due to the lower content of phenols of higher volatility such as phenol and p-cresol. It was also noted that as the water content in the gas stream increased, the phenolic content in the bio-oil increased from 42 to 98% weight of total bio-oil mass. This was lower than the trend of scenario 1 due to the differences in composition of their respective bio-oils. The process analysis showed that the optimum value of the condenser temperature is critical for the production of the concentrated phenolic solution. Since the water content in the concentrated phenolic solution needs to be as low as possible, the optimum condenser temperature is determined at the intersection of the heat loss trend with the phenolic losses trend. For scenario 1, the optimum temperature is 80°C whilst for scenario 2 it is 86°C. The corresponding phenolic concentration at the respective optimum temperatures were

97% weight and 96% weight respectively. The optimum temperatures were based only on process parameters, but the optimum temperature that incorporates the costs of the process is greater practical value.

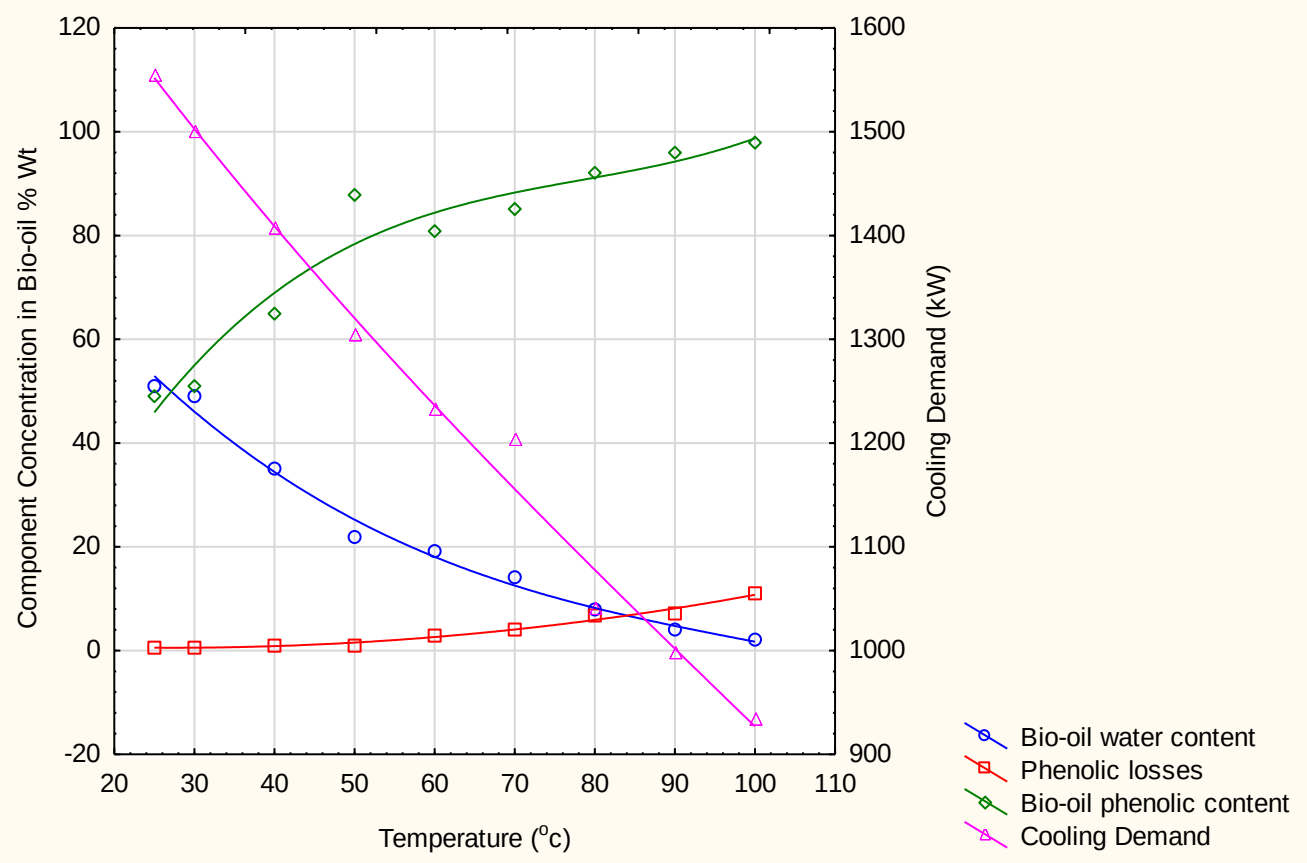


Figure 26 Variation of several parameters with condenser temperature for Scenario 2

4.1.4 Process analysis of phenolic solution distillation columns

This section discussed the effect of several parameters on the performance of the Pre-Flash column and the fractionation column. Since pre-flash unit serves the main purpose of removing residual water, main parameters that directly affect the amount of residual water removed such as reflux ratio and number of trays are discussed. Also parameters that affect the phenolic fractions produced in the fractionation column are discussed.

Table 16 below gives a summary of the modelling results obtained in this study for the fractionation of the phenolic mixture as described in scenario 3 and 4.

Table 16 Summary of the optimum operating parameters for the Pre-flash column and the fractionation column for scenario 3 and 4

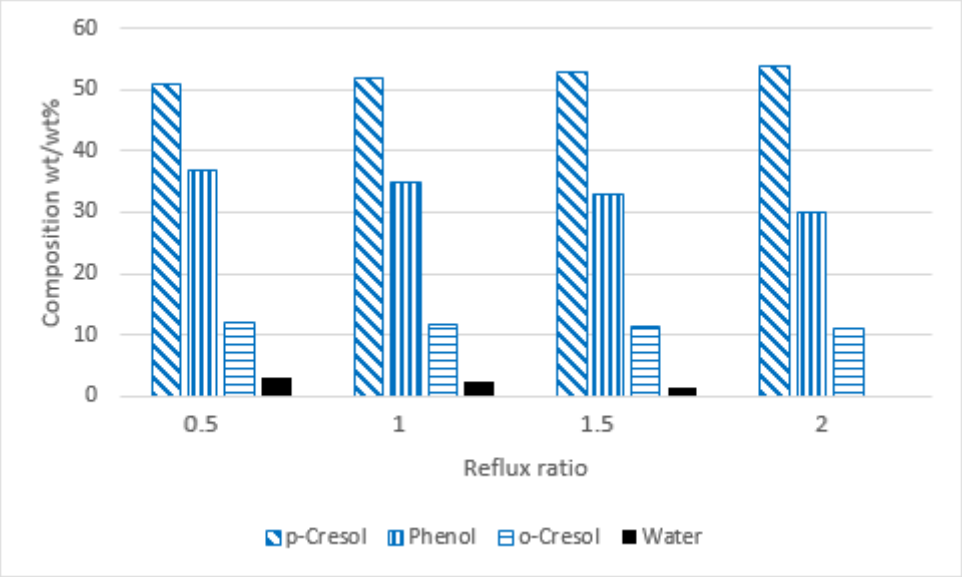
Parameter	Scenario 3	Scenario 4
Pre-flash unit		
Reflux ratio	1.5	1.5
Number of trays	15	15
Feed trays position	13	14
Cresol Flowrate (kg/hr)	29.9	30.4
Fractionation column		
Reflux ratio	2	2
Number of trays	25	32
Feed plate position	23	23
Syringaldehyde fraction flowrate (kg/hr)	75	76
Guaiacol fraction flowrate (kg/hr)	100.1	110
Syringol fraction flowrate (kg/hr)	99.9	99
Creosote (kg/hr)	2345	2356
Energy Demand (MW)	6.3	6.7
Cooling demand (MW)	6.7	6.9

From Table 16, comparison of design variables of scenario 3 to scenario 4 shows that the amounts of phenolic fractions produced are relatively similar for syringol and syringaldehyde fractions. The main difference is the amount of cresol, guaiacol and creosote fraction produced which are 4, 5 and 6% respectively greater for scenario 4. This was mainly due to the difference in yields of the individual phenolic compounds in the bio-oil produced by each specific catalyst in the lignin pyrolysis reactor. The energy demands show that scenario 4 needs 0.1MW more for cooling and 0.2MW more boiler duty than scenario 3. The difference in reboiler duty is mainly due to a higher oligomer and phenolic content in the bio-oil fed into the fractionation column for scenario 4 that requires more energy due to the increase in specific heat capacity.. This is also evident in the higher condenser duty that is attributed to a more phenolic distillate produced since the reflux ratios between the two scenarios are similar. The

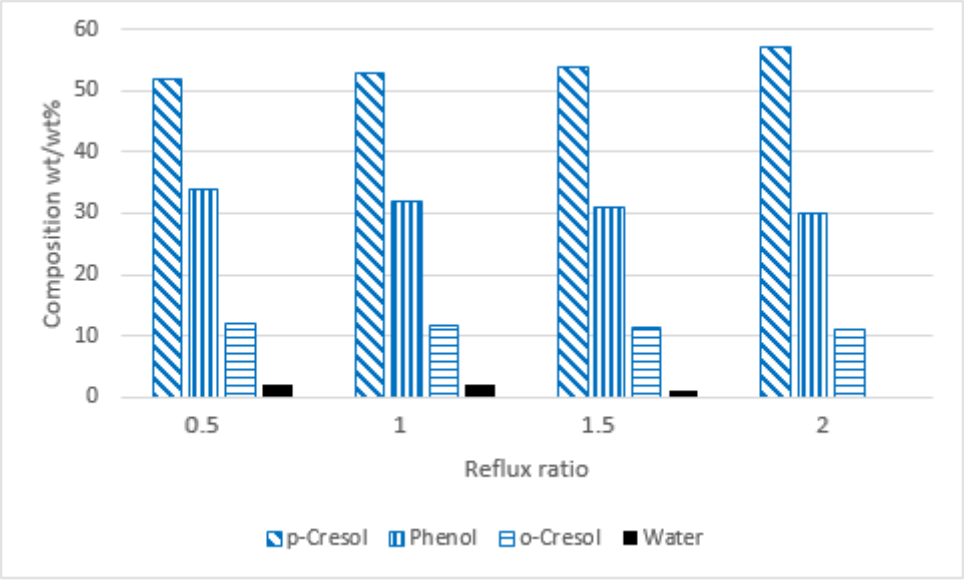
two reboilers of the phenol fractionation plant have an energy demand for scenario 3 of 6.3 MW whilst for scenario 4 it is 6.7 MW. When the excess energy from the pyrolysis reactor is sent to the reboiler, the heat utilities decrease to 1.26 MW and 1.35 MW for scenario 3 and scenario 4. Since the reboilers are operating at the boiling point of the phenolic compounds (i.e. 230^{o}C), high pressure can be used to supply the residual energy required in the reboiler. In order to investigate the effect of change of the variables in Table 16, a sensitivity analysis was performed and discussed.

4.1.4.1 Effect of the reflux ratio on the Pre-flash unit

When the reflux ratio increases, the number of trays decreases. Thus in order to determine the effect of reflux ratio of the product specification, the Aspen Plus® design specification tool was used to vary them so to meet the product specification of this light end fraction (CRESOL) shown in Table 5. For scenario 3 and 4, the variation of the reflux ratio with product specification is shown in Figure 27.



(a)



(b)

Figure 27 Effect of the reflux ratio on the Pre-flash unit for (a) scenario 3 (b) scenario 4

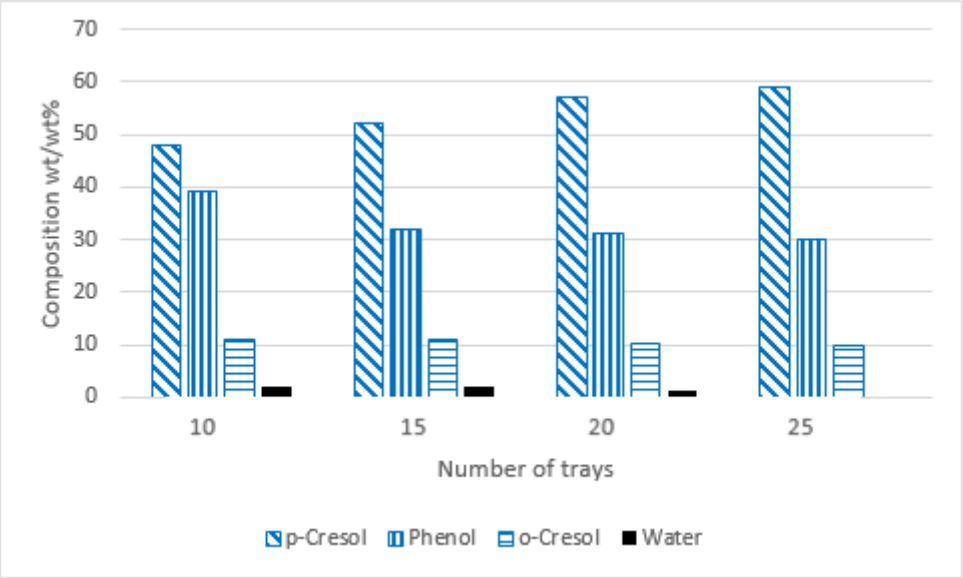
It was noted that as the reflux ratio increased from 0.5 to 2, the composition of the cresol fraction had an increase in composition of p-cresol and phenol from 52 to 60 Wt. % of distillate and 40 to 38 Wt. % of distillate respectively. Since increase in reflux ratio results in better separation within the column, the water content in the cresol fraction decreased from 6 to 1Wt. % of distillate. This decrease in water content to the free water stream showed that the Pre-flash column reduced the water content of the concentrated phenolic solution from 7 to 0Wt. % of distillate.

For the case of scenario 3, the same procedure for process analysis as in scenario 3 was applied in Figure 26. It was noted just as in the scenario 3 when the reflux ratio increased, that the compositions of the phenols in the cresol fraction increased respectively. But for the scenario 4, as the reflux ratio increased from 0.5 to 2, composition of the cresol fraction had an increase in composition of p-cresol and phenol from 53 to 58Wt. % of distillate and 34 to 30Wt. % of distillate respectively. The water also decreased from 6 to 0Wt. % of distillate.

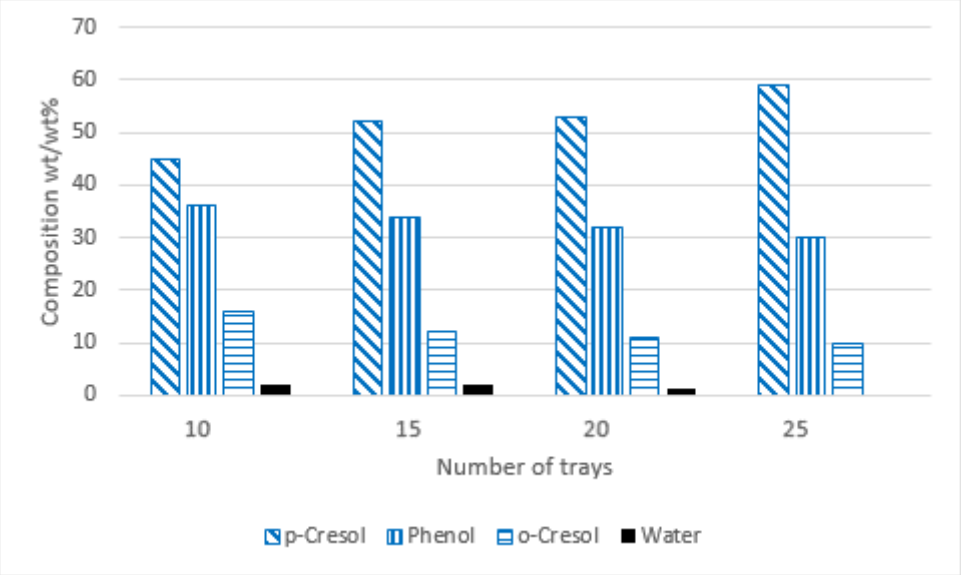
4.1.4.2 Effect of the number of trays on the Pre-flash unit

In order to determine the effect of the number of trays, the Aspen Plus® design specification tool was also employed by varying the number of plates so to meet the

product specification of this light end fraction cresol. For scenario 3, the process analysis is shown in Figure 28(a), whilst for scenario 4 it is shown in Figure 28(b).



(a)



(b)

Figure 28 Effect of the number of trays on the Pre-flash unit for (a) scenario 3 (b) scenario 4

Since number of trays is representative of the separation efficiency of the column, the higher the number of trays, the higher the efficiency. Hence for scenario 3, it was noted that as the number of trays increased from 10 to 25, the composition of the phenols in the cresol fraction also increased. For scenario 3, composition of the cresol

fraction had an increase in composition of p-cresol and phenol from 48 to 59Wt. % of distillate and 39 to 30Wt. % of distillate respectively. For scenario 4, composition of the cresol fraction had an increase in composition of p-cresol and phenol from 45 to 60Wt. % of distillate and 35 to 30Wt. % of distillate respectively. When the concentrated phenolic solution exits the Pre-flash, it contains phenols that have lower volatility. These phenols were fractionated in the fractionation column FRACT into fractions according to the product specifications shown in Table 5.

4.1.4.3 Effect of the feed rate on the fractionation column

The same procedure of using the Aspen Plus® design specification tool in optimisation of the Pre-flash was applied in determining the optimum reflux ratio and number of trays and the optimum values for the fractionation column and the values of these variables are shown in Table 16. The section analyses the effect of feed rate, feed tray position, boiler duty and condenser duty on the phenolic fractions and the number of stage of the fractionation column. Since phenolic fractions are produced in scenario 3 and 4, the discussion is focused on the effect of these variables on the fractionators in both scenarios. Table 17 illustrates the effect of the feed rate on the composition of the phenolic fractions.

Table 17 Effect of rate of feed on the fractionation column

Feed rate (kg/hr)	**Concentration of phenolic fractions**			
	Cresol	Guaiacol	Syringol	Syringaldehyde
756	0.344	0.324	0.345	0.123
569	0.234	0.233	0.234	0.102

It can be seen that in both scenarios, as the feed flow rate increases, the composition of the lighter ends in the bottom plate decrease whilst for the heavy phenolic components decrease in the upper plate. When the feed rate is increased, the residence time of the vapours in the column also decreases thus causing inefficient separation and a reduction in the percentage purity of the targeted phenolic

compounds. Also increasing feed rates, increases vapour flowrates that in turn cause flooding due to increased liquid hydrostatic pressure.

At lower feed rate, there is a reduction of the lighter ends in the residue stream and the heavier ends in the distillate. This in turn results in long vapour residence times in the column thus enabling a higher separation efficiency and percentage purity of the phenolic fractions. However, decreasing the feed flow rates results in decreased flow rates of the targeted phenolic fractions product streams, mainly due to the high vapours pressure than is gravitational flow of the downstream flow rate liquid that causes weeping on the trays and reduced efficiency of the column.

4.1.4.4 Performance of the fractionation column

Figure 29 shows how the phenolic fractions vary within the stages of the fraction column (FRACT) where stage 1 is the top tray whilst stage 20 is the bottom tray.

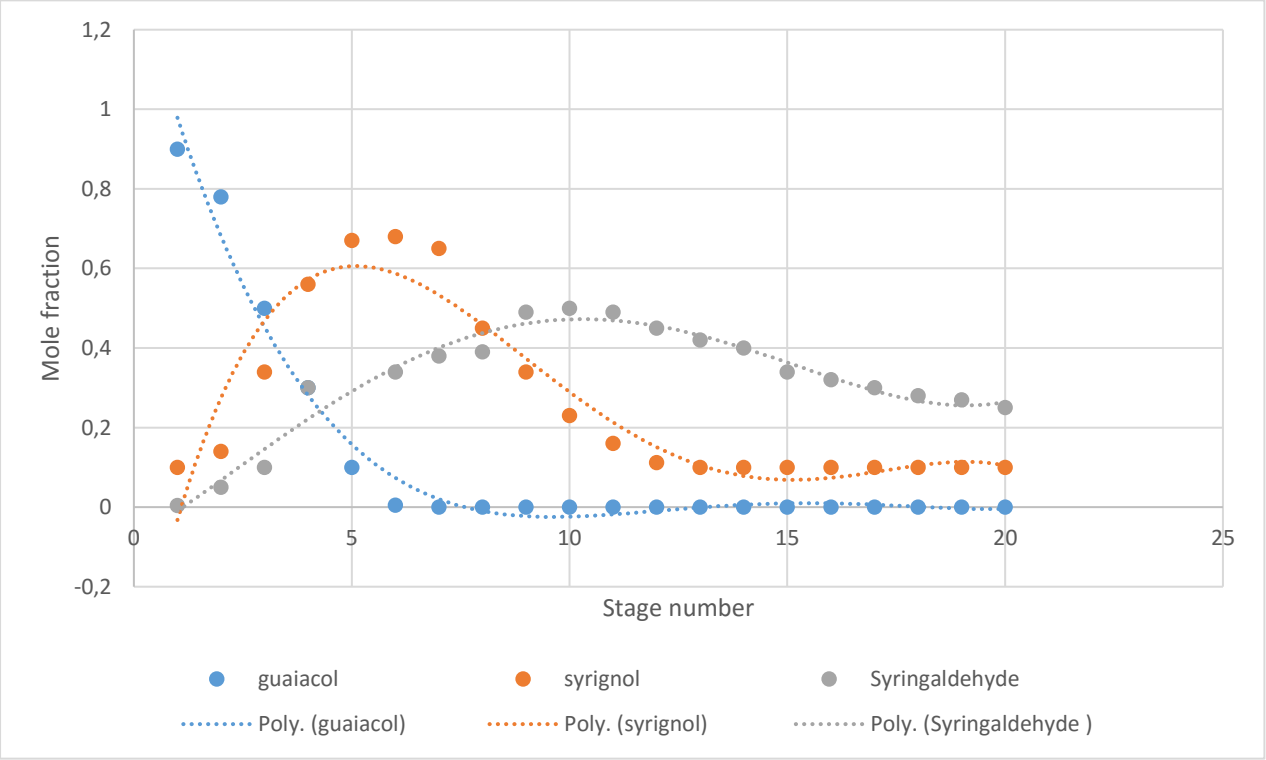


Figure 29 Performance of the fractionation column

It was noted that the fractionator was able to separate high boiling phenolic compounds such as cresol, and guaiacol into the distillate. Since the desired phenolic fraction has to be withdrawn at a plate where its fraction is at maximum

concentration, the suitable trays of withdrawal were found to be 1, 5 and 10 for the guaiacol, syringol and syringaldehyde fractions respectively. But it is worth noting a fraction of syringol and syringaldehyde is lost to the bottom tray (i.e. residue stream with creosote) as evidenced their mole fractions that are not zero.

4.2 Economic and Environmental Impact Analysis

Summary results of the economic modelling of the four scenarios studied in this project are presented with all cost data reported in US$ (year 2016). For each scenario, the economic results include fixed investment cost, operating cost, product sales revenues as well as the summary of the profitability indicators such as IRR.

4.2.1 Capital and operating costs

Table 18 below shows a summary of the capital and operating costs of each scenario.

Table 18 Capital and operating costs of the four scenarios

	Scenario 1	Scenario 2	Scenario 3	Scenario 4
Investment (US$ Millions per year)				
Total Fixed costs	32.13	36.04	33.57	37.48
Total indirect costs	19.28	21.62	20.14	22.49
Total fixed capital	41.13	53.66	53.71	59.97
Production costs (US$ Millions per year)				
Total Variable costs	2.71	2.46	3.37	2.62
Total fixed operating costs	2.77	2.98	2.89	3.03
Sales revenue (US$ Millions per year)				
Total Sales	14.77	12.96	19.90	17.55
Economic indicator				
IRR (%)	1.10	2.07	19.35	18.23

Table 18 above shows the breakdown of the TCI requirement of the various phenol production scenarios. A comparison of TCI shows that production of the crude phenolic mixture (i.e. creosote) results in the lowest TCI, indicated by the US$51.1 million TCI cost for scenario 1. Although both scenario 1 and 2 produce crude phenolic

mixture, the TCI of scenario 2 is significantly higher mainly due to the bulk of catalyst that remains within the reactor as the catalyst is recycled back to the reactor after regeneration. The bulk of the catalyst that remain in the reactor needs to be accounted for. Since it is within the reactor, it is considered as part of the capital costs of the reactor. Thus the cost of catalyst used to fill the reactor has significant effect on the CAPEX due to the relatively high price of the zeolite catalyst (i.e. US$850 per tonne). The same effect is seen in scenario 3 and 4. When scenario 1 and 2 were compared to scenario 3 and 4, it was noted that the TCI increased by 4.4% and 4.0% for scenario 1 and 2 respectively. This minor increase indicates that the TCI of the reactor is the major contributor to the TCI in all scenarios. Also this marginal increase shows that that the phenol fractionation section of the plant is marginally small in size compared to the pyrolysis reactor. Thus a reduction in TCI of the reactor is beneficial in lowering the risk factor associated with attracting investment for the plant. Also lower TCI makes it for the bio-refinery to grow in terms of diversification of its product offerings.

Breakdown of the productions costs shows a different trend to that seen in comparison of the TCI. It can be seen from Table 18 that the scenarios 1 and 3 have Total Variable Costs (TVC) of US$2.92 million per year whilst in scenario 2 and 4 it is US$8.38 million per year. The variable costs are significantly different due to the difference in cost of catalyst. Scenarios 1 and 3 use sodium hydroxide (that has a market value of US$300/ton), whilst scenario 2 and 4 use zeolite (that has a market value of US$ 850/ton). Since the catalyst is discarded together with ash in scenario 1 and 3, disposal costs are higher compared to scenario 2 and 4 where the catalyst is recycled. Cost of catalyst has a significant effect on the total variable costs unlike other costs such as raw material that remains unchanged for all scenarios at US$0.78 million per year. Since labour, insurance are some of the fundamental costs necessary for the continual operation of a plant, the Total Fixed Costs of scenario 1 and 3 was found to be US$2.84 million whilst for scenario 2 and 4 was US$2.89 million. This is an indication that in all scenarios, the same number of people is needed for labour and

also the insurance costs are relatively the same. This indicates that reduction in operating costs in the operation of the pyrolysis reactor can significantly reduce the overall production costs in all scenarios thus increasing the returns on investment.

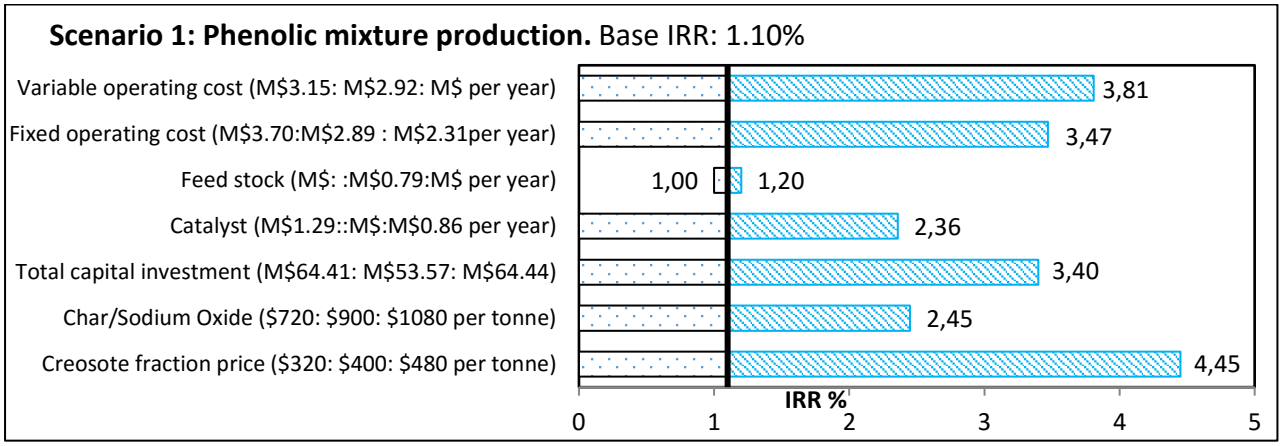
Revenue that is generated from the produced phenolic fractions comes in the form of sales revenue (inclusive of main products revenue and by-products revenue). It can be seen from Table 18 that the Total Sales Revenues for scenario 3 and 4 are significantly higher than those of scenario 1 and 2. This is mainly due to the significant differences in the market prices produced in each scenario. Scenario 1 and 2 produce creosote that has a market value of US$ 650 per ton whist scenario 3 and 4 produce phenolic fractions with a market value of US$6000. It is worth noting there are differences in total sales between scenario 1and 2 and also scenario 3 and 4. This is mainly due to the differences in production volumes of the phenolic fraction in each scenario.

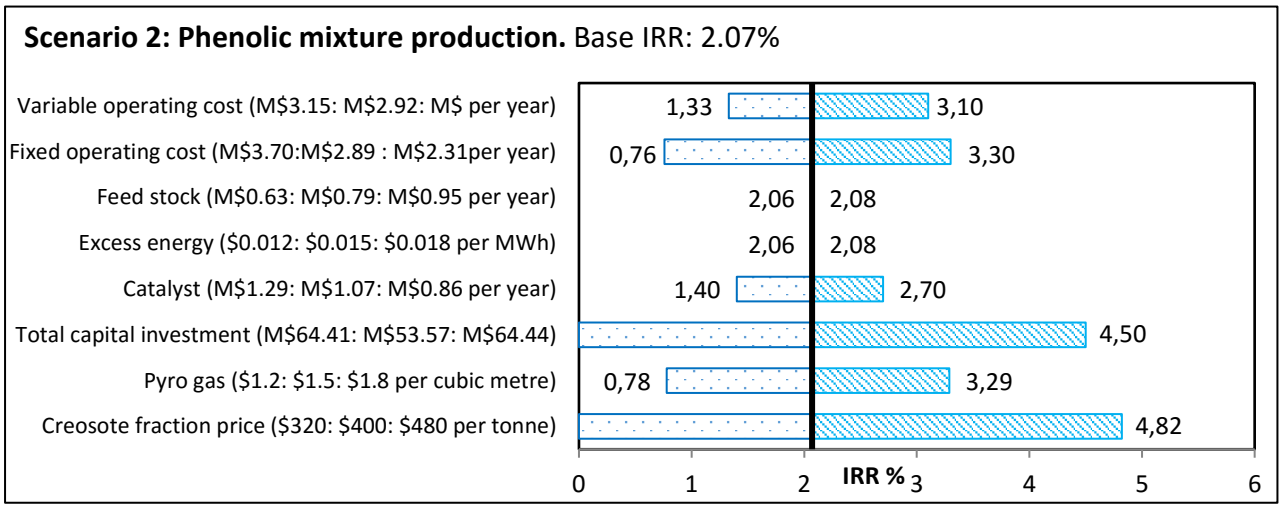
Due to the varying TCI and the production costs between the four scenarios, the economic performance of each scenario is indicated by using the IRR. As seen from Figure 30, the IRR for scenario 3 and 4 are significantly higher than the IRR of scenario 1 and 2. IRR of scenario 1 and 2 was 11.92 and 8.2% respectively. Scenario 1 had a higher IRR than scenario 2 due to the higher sales volumes associated with the sales of the by-products. Scenario 3 and 4 were both attractive in terms of funding as they have significantly higher IRR values but scenario 3 is more economically viable. The difference between the two scenarios is that the scenario 3 has a higher IRR (i.e. 21%) than scenario 4 that has IRR of 18.23%. Although both scenarios produce phenolic fractions that have higher market values than the phenolic product in scenario 1 and 2, scenario 3 has higher IRR due to the additional sales volumes associated with the by-product sodium oxide. The variable costs are significantly different due to relative difference in terms of costs of catalyst. Scenarios 1 and 3 use sodium hydroxide (that has a market value of US$300/ton), whilst scenario 2 and 4 use zeolite (that has a market value of US$ 850/ton). Since the catalyst is discarded together with ash in

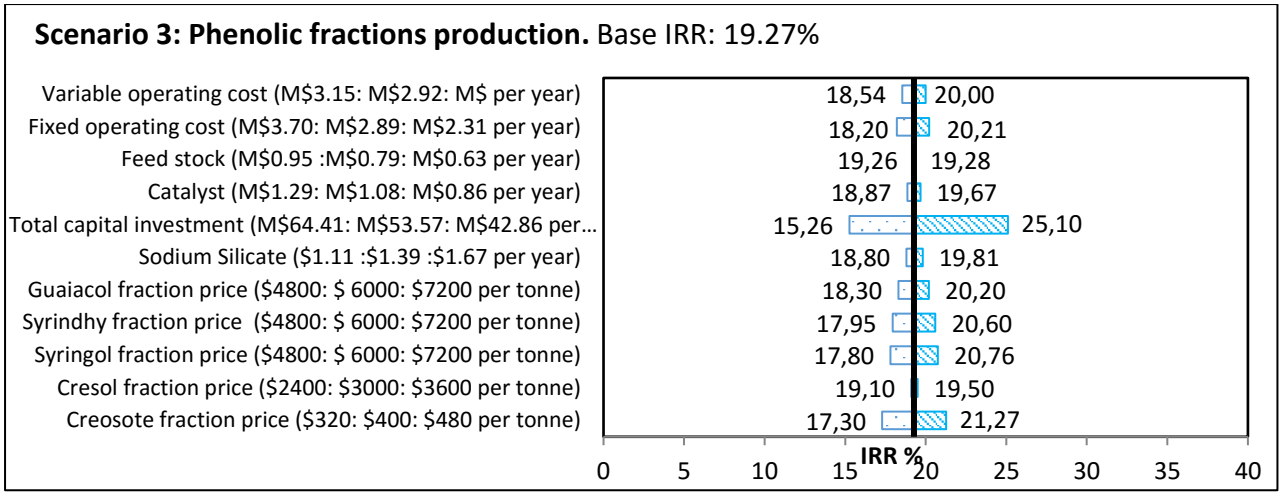
scenario 1 and 3, disposal costs are higher compared to scenario 2 and 4 where the catalyst is recycled.

4.2.2 Sensitivity analysis

Profitability indicators of the various phenol models depend on parameter choices such as the variable operating costs, feedstock, catalyst, TCI and phenolic fractions selling prices. A sensitivity analysis was thus used to study the effects of changes on these parameters on the overall economics of the various phenolic compound production scenarios.







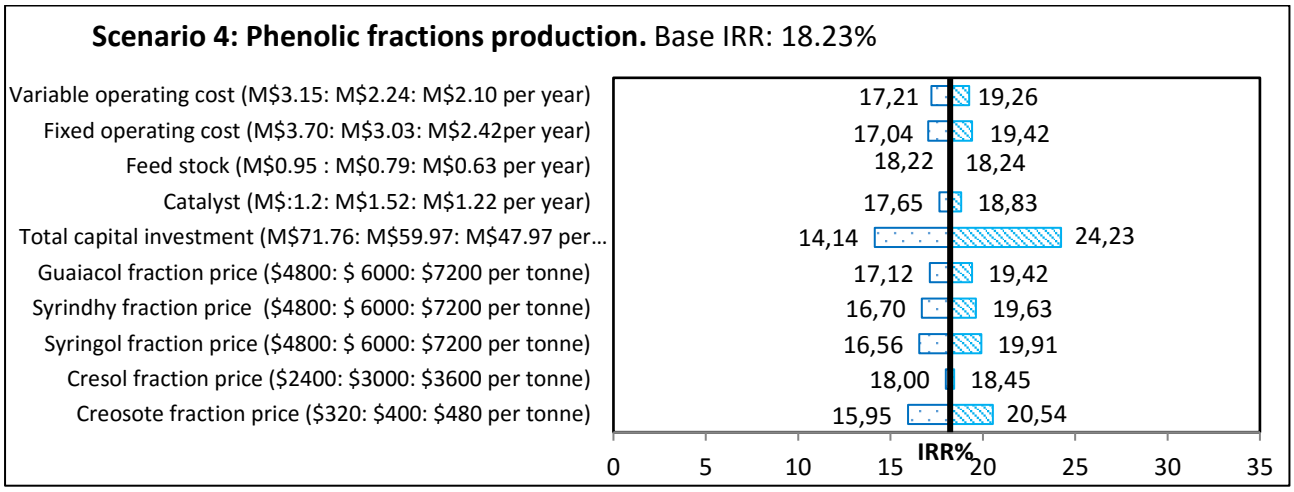


Figure 30 Economic sensitivity analysis of the investigated scenarios

Figure 30 illustrates the sensitivity analysis for the four scenarios. The scenario 3 had the highest IRR of 19.27% whilst scenario 2 had lowest IRR of 1.10%. In all the processes, variation in phenolic fraction market prices caused varying changes in IRR. The parameter that had significant effect on IRR is the TCI whilst the parameter with the least effect on the IRR was found to be the feedstock price.

In the case of scenario 1, assessment of the variables that generate income showed that when the market price of creosote and char/sodium hydroxide mixture were increased by 20%, the IRR increased by 1.35% and 3.35% respectively. When the market price of creosote andchar/sodium hydroxide mixture were decreased by 20%, the IRR decreased by zero in both cases.

In the case of scenario 2, assessment of the variables that generate income shows that when the market price of creosote, pyro-gas and excess energy were increased by 20%, the IRR increased by 2.75, 1.22 and 0.01% respectively. When the market price of creosote, pyro-gas and excess energy decreased by 20%, the IRR decreased by 2.07, 1.29 and 0.01% respectively. In the case of scenario 3, the parameter that had a major effect on IRR is the TCI whilst the parameter with the least effect on the IRR was found to the feedstock price. Also it can be seen that when the market price of the phenolic fractions increased by 20%, increased the IRR by 1.49%, 1.33%, 0.93%, 0.23% and 2.00% for phenolic fractions syringol, syringaldehyde, guaiacol, cresol and creosote respectively. When the market prices of the phenolic fractions were decreased by 20%, the IRR decreased by 1.47%, 1.32%, 0.97%, 0.17% and 1.97% for phenolic fractions syringol, syringaldehyde, guaiacol, cresol and creosote respectively. Although creosote has the lowest market price (i.e. US$ 400per tonne), its change in market price had significant effect on the IRR due to high production volumes. The change in market price of the syringaldehyde fraction had significant effect on the IRR mainly due to its high market value and relatively high production volumes. Since catalyst is one of the components that is given high priority during chemical processing, the effect of the change of the catalyst price was found to have a significantly low effect on the IRR. It was noted that when the catalyst price was decreased by 20%, the IRR decreased by 0.6%. When the catalyst price was increased by 20%, the IRR increased by 0.4%. This was due to the relativity low market price of the catalyst that caused the variable cost to remain relatively low despite the change in price of the catalyst.

In the case of scenario 4, just as in scenario 3, TCI had a major effect on the IRR whilst the parameter with the least effect on the IRR was found to be the feedstock price. Also it can be seen that when the market price of the phenolic fractions increased by 20%, the IRR increased by 1.68%, 1.40%, 1.11%, 0.22% and 2.31% for phenolic fractions syringol, syringaldehyde, guaiacol, cresol and creosote respectively. When the market prices of the phenolic fractions were decreased by 20%, the IRR decreased by 1.57%, 1.53%, 1.19%, 0.23% and 2.23% for phenolic fractions syringol,

syringaldehyde, guaiacol, cresol and creosote respectively. Although creosote has the lowest market price (i.e. US$ 400 per tonne), its change in market price had significant effect on the IRR due to high production volumes. The change in market price of the syringaldehyde fraction had significant effect on the IRR mainly due to its high market value and relatively high production volumes. Since catalyst is one of the components given high priority during chemical processing, the effect of the change of the catalyst price had significantly low effect on the IRR. It was noted that when the catalyst price was decreased by 20%, the IRR decreased by 0.58%. When the catalyst price was increased by 20%, IRR increased by 0.60%. Although the price of the catalyst was relatively high (US$850 per tonne), recycling the catalyst enabled the variable cost associated with the change in price of the catalyst to remain low over the 25 year period of the plant.

4.3 Environmental Impact (CO_2 emissions) Analysis

Table 19 Summary of CO2 emissions of the scenarios

Parameter	Baseline	Scenario 1	Scenario 2	Scenario 3	Scenario 4
CO_2 emissions (kg/ kg phenol)	4.15	1.80	2.24	2.60	2.72

It can be seen from Table 19 that all four investigated scenarios had lower CO_2 emissions compared to the baseline (i.e. emissions of fossil based phenols). Scenario 1, 2, 3 and 4 emitted 56.6, 46.02, 37.34 and 34.45% less CO_2 than the baseline respectively. Scenario 2 was found to emit more 0.44 kg CO_2 per kg phenol than scenario 1 due to the fact that all the char had to be combusted in order to regenerate the catalyst. Scenario 4 was found to emit more 0.12 kg CO_2 per kg phenol more than scenario 3 mainly due to the deference in CO2 emissions associated with the imported energy.

4.4 Impact of Study

The study showed production of phenolic fractions via scenario 3 is the desired economic route but it produced higher emissions than scenario 1 and 2. From a social

impact perspective, it can be seen that a total of 16 jobs could be created in all four scenarios. The job creation from this study will have an impact on the agricultural sector where more labour will be hired in order to collect field residue and trash that can be converted to phenols. This is particularly the case in South Africa and rest of Africa where manual labour is cheaper and more abundant than in Europe and America. Since the South African government is currently lobbying for the private sector to create jobs, this is a sustainable initiative as bio-residue is abundant in the South African agricultural sector.

CHAPTER 5

CONCLUSIONS and RECOMMENDATIONS

5.1 Conclusion

The objective of this study was to evaluate the economically worthy to convert lignin into value added chemicals rather than just burn it to generate energy. This was performed by determining the economic viability of four scenarios for producing phenols from lignin via pyrolysis process. Mass and energy balances from the lignin pyrolysis and phenol fractionation Aspen Plus® models were applied to calculate the CAPEX and OPEX associated with each scenario.

Process analysis showed that the model is valid between the temperatures of 400 and 800^{o}C (i.e. the pyrolysis temperature range in the literature). Although there are some variations between the model results and the experimental results, the prediction of the model can be greatly improved if mathematical models that predict re-isomerisation of the phenolic compounds during pyrolysis can be deduced from experimental data. The optimum condenser temperature for fractional condensation that could minimise the phenolic losses whilst keeping the heat loss low should be above 80^{o}C. Also the concentration of the phenols in the concentrated phenolic solution on average increased from 45 to 93% weight bio-oil as the condenser temperature increased from 25 to 100^{o}C. Fractionation of the concentrated phenolic solution showed that the suitable reflux ratio for the pre-flash and fractionation unit should lie between 1.5 and 2 so as to produce the required separation. Also the number of trays needed for separation should be above 20 in both scenarios in order to achieve separation and product specification. Although these optimum parameters were based on process parameters, it was seen that it is necessary to determine optimum values of these parameter based on combined process and economic analysis for commercial production of the phenolic products.

The economic indicators were determined via cash flow discount by determining the IRR for the four scenarios based on the market prices of the phenolic fractions and the

economic assumptions. Thereafter the scenarios of producing phenols were compared. The economic analysis showed that scenario 3 was more economically feasible than the other three scenarios as it had the highest IRR of 19.27%. Production of crude phenolic solution (creosote) had generated the lowest IRR where scenario 1 and 2 had IRR values of 1.10 and 2.07% respectively. The economic analysis showed that it is economically feasible to produce a phenolic mixture using a cheap catalyst provided there is a by-product that will increase the sales volumes. Production of phenolic fractions from lignin was found to be economically feasible for both scenario 3 and 4. Phenolic fraction production using a cheap catalyst as it produced an IRR of 19.27%. Production of phenolic fractions from pyrolysis of lignin using a catalyst of high market value was economically viable as it produced an IRR of 18.25% which was mainly due to the high production costs associated with using a catalyst of high market value. Thus it can be concluded that production of phenolic fractions from lignin is more economic viable route but the yields of the phenolic compounds have to increase above the current 1wt % lignin so as increase the market value of the phenolic fractions. This will also increase the IRR of the project thus attracting more investment. In addition the CO_2 revealed that it was more environmentally friendly to produce lignin based phenols compared to fossil based phenols.

5.2 Recommendations

It is recommended that a comprehensive LCA must be conducted so as to determine if bio-phenols are indeed environmentally friendly compared to fossil-based phenols. Due to the low production rates of the phenolic products generated by the pyrolysis based models, it is recommended that the use of bagasse to produce the lignocellulose residue be supplemented by harvest residues and tops. This would ensure that enough lignin is made available for conversion phenol models. It is also recommended that pilot studies be performed so as to validate the commercial viability of producing phenolic fractions from lignin.

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APPENDIX

A1 Catalytic pyrolysis of lignin into a phenolic mixture using sodium hydroxide catalyst

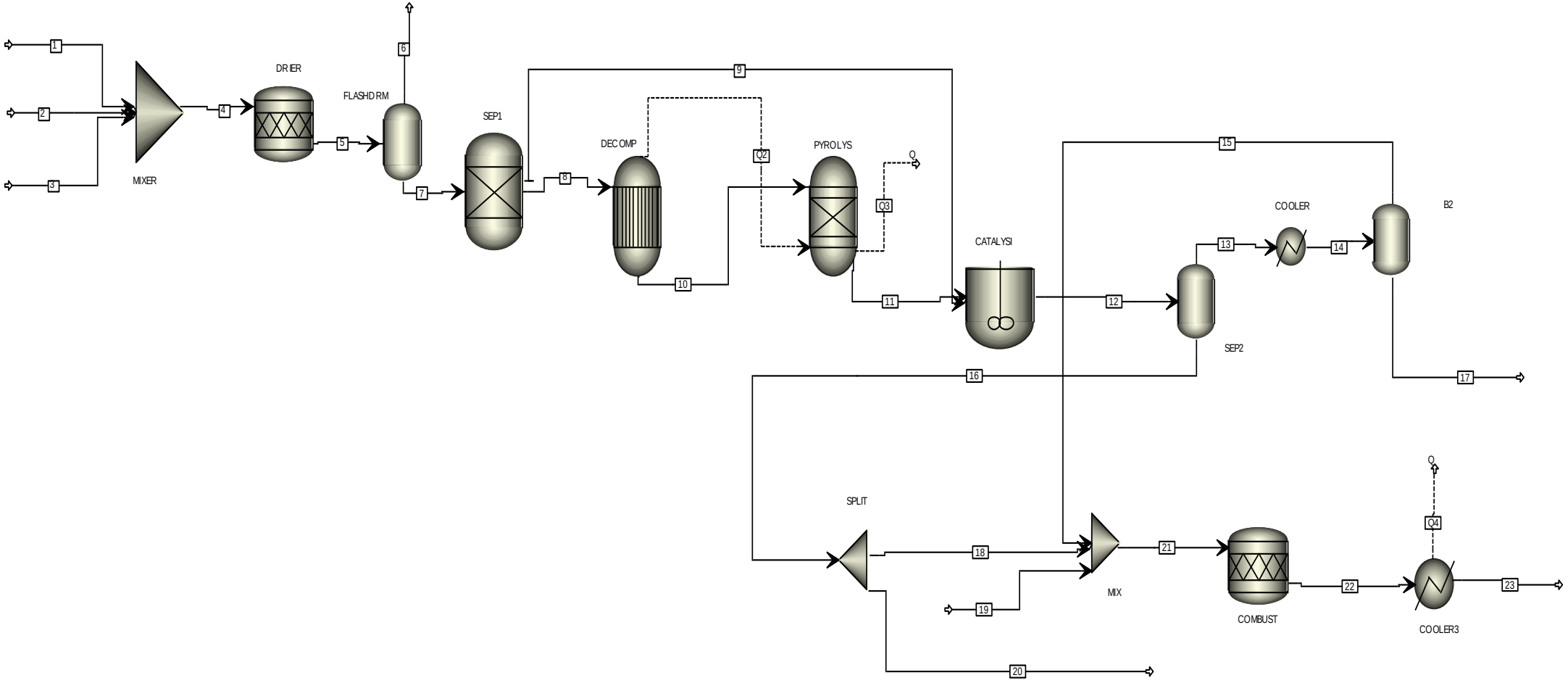

Figure 31 Catalytic pyrolysis of lignin into a crude phenolic using sodium hydroxide catalyst

Stream	1	2	3	4	5	6	7	8	9	10
Mass Flow kg/hr										
LIGNIN	5525.00	0.00	0.00	5525.00	4998.90	0.00	4998.90	4998.90	0.00	0.00
WATER	0.00	2763.00	0.00	2763.00	526.10	526.10	0.00	0.00	0.00	499.89
CATALYST	0.00	0.00	552.50	552.50	552.50	0.00	552.50	0.00	552.50	0.00
CARBON	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2298.54
HYDROGEN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	295.13
OXYGEN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1877.89
SULPHUR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.90
ASH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	19.80
CARBON DIOXIDE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NITROGEN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6.75
METHANE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PHENOL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P- CRESOL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STEAM	0.00	0.00	0.00	0.00	2763.00	2763.00	0.00	0.00	0.00	0.00
EUGENOL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GUAIACOL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
O-CRESOL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GUAIACOL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
METHY-PHENOL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SYRINGOL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SYRINGALDEHYDE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ACETOVANNILONE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OLIGOMERS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Flow kg/hr	5525.00	2763.00	552.50	8840.50	8840.50	3289.10	5558.40	4998.90	552.50	4998.90
Temperature C	25.00	25.00		20.65	100.00	100.00				500.00
Pressure bar	1.00	1.00	1.00	0.00	1.00	1.00	1.00	1.00	1.00	1.00
Enthalpy MW	-20.78	-12.18	56.00	-10.31	-12.14	-12.14	-67.00	-56.00	-46.00	-0.92
Entropy J/kg-K		-9055.61	-3074.76	2825.99	-1836.48	-1836.48	-2885.90	-2885.90	-2885.90	2723.40

Stream	11	12	13	14	15	16	17	18	19	20
Mass Flow kg/hr										
LIGNIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
WATER	2216.42	2216.42	2216.42	2216.42	228.81	0.00	1987.62	0.00	0.00	0.00
CATALYST	0.00	552.50	0.00	0.00	0.00	552.50	0.00	552.50	0.00	552.50
CARBON	1435.12	1435.12	0.00	0.00	0.00	1435.12	0.00	717.56	0.00	717.56
HYDROGEN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OXYGEN	206.39	206.39	206.39	206.39	205.71	0.00	0.68	0.00	243.00	0.00
SULPHUR	0.90	0.90	0.90	0.90	0.00	0.00	0.90	0.00	0.00	0.00
ASH	19.80	19.80	0.00	0.00	0.00	19.80	0.00	9.90	0.00	9.90
CARBON DIOXIDE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NITROGEN	6.32	6.32	6.32	6.32	6.30	0.00	0.02	0.00	456.00	0.00
METHANE	138.66	138.66	138.66	138.66	137.79	0.00	0.88	0.00	0.00	0.00
PHENOL	6.71	6.71	6.71	6.71	0.55	0.00	6.16	0.00	0.00	0.00
P-CRESOL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STEAM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
VANILLIN	11.87	11.87	11.87	11.87	0.00	0.00	11.87	0.00	0.00	0.00
O-CRESOL	2.00	2.00	2.00	2.00	0.13	0.00	1.87	0.00	0.00	0.00
GUAIACOL	16.42	16.42	16.42	16.42	0.02	0.00	16.40	0.00	0.00	0.00
ETHYL- PHENOL	10.47	10.47	10.47	10.47	0.00	0.00	10.47	0.00	0.00	0.00
METHY-PHENOL	0.69	0.69	0.69	0.69	0.03	0.00	0.67	0.00	0.00	0.00
SYRINGOL	10.48	10.48	10.48	10.48	0.01	0.00	10.47	0.00	0.00	0.00
SYRINGAHYDE	13.70	13.70	13.70	13.70	0.00	0.00	13.70	0.00	0.00	0.00
ACETOVANNILONE	5.42	5.42	5.42	5.42	0.00	0.00	5.42	0.00	0.00	0.00
OLIGOMERS	860.80	860.80	860.80	860.80	0.00	0.00	860.80	0.00	0.00	0.00
Total Flow kg/hr	4998.58	5551.08	3543.66	1327.24	579.34	2007.41	2964.32	1279.96	0.00	1279.96
Temperature C	500.00	500.00	600.00	100.00	80.00		80.00		25.00	
Pressure bar	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Enthalpy MW	-7.80	-7.80	-7.58	-9.03	-1.02	-56.00	-9.03	-45.00	0.00	-43.00
Entropy J/kg-K	-672.88	-672.88	-400.53	-3214.74	-1450.86	-1808.90	-6930.93	-1808.90	140.04	-1808.90

Stream	21	22	23
Mass Flow kg/hr			
LIGNIN	0.00	0.00	0.00
WATER	228.81	539.03	539.03
CATALYST	552.50	552.50	552.50
CARBON	717.56	0.00	0.00
HYDROGEN	0.00	0.00	0.00
OXYGEN	243.00	243.00	243.00
SULPHUR	0.00	0.00	0.00
ASH	9.90	9.90	9.90
CARBON	0.00	3009.50	3009.50
NITROGEN	456.00	456.00	456.00
METHANE	137.79	0.00	0.00
PHENOL	0.55	0.00	0.00
P-CRESOL	0.00	0.00	0.00
STEAM	0.00	0.00	0.00
VANILLIN	0.00	0.00	0.00
O-CRESOL	0.13	0.13	0.13
ETHYL- PHENOL	0.00	0.00	0.00
METHY-PHENOL	0.03	0.03	0.03
SYRINGOL	0.00	0.00	0.00
SYRINGAHYDE	0.01	0.01	0.01
ACETOVANNILONE	0.00	0.00	0.00
OLIGOMERS	0.00	0.00	0.00
Total Flow kg/hr	2346.29	4810.11	4810.11
Temperature C	113.19	900.00	120.00
Pressure bar	1.00	1.00	1.00
Enthalpy MW	178.56	-19.00	-18.00
Entropy J/kg-K	403.92	1611.48	422.42

A2 Catalytic pyrolysis of lignin into a crude phenolic mixture using zeolite catalyst

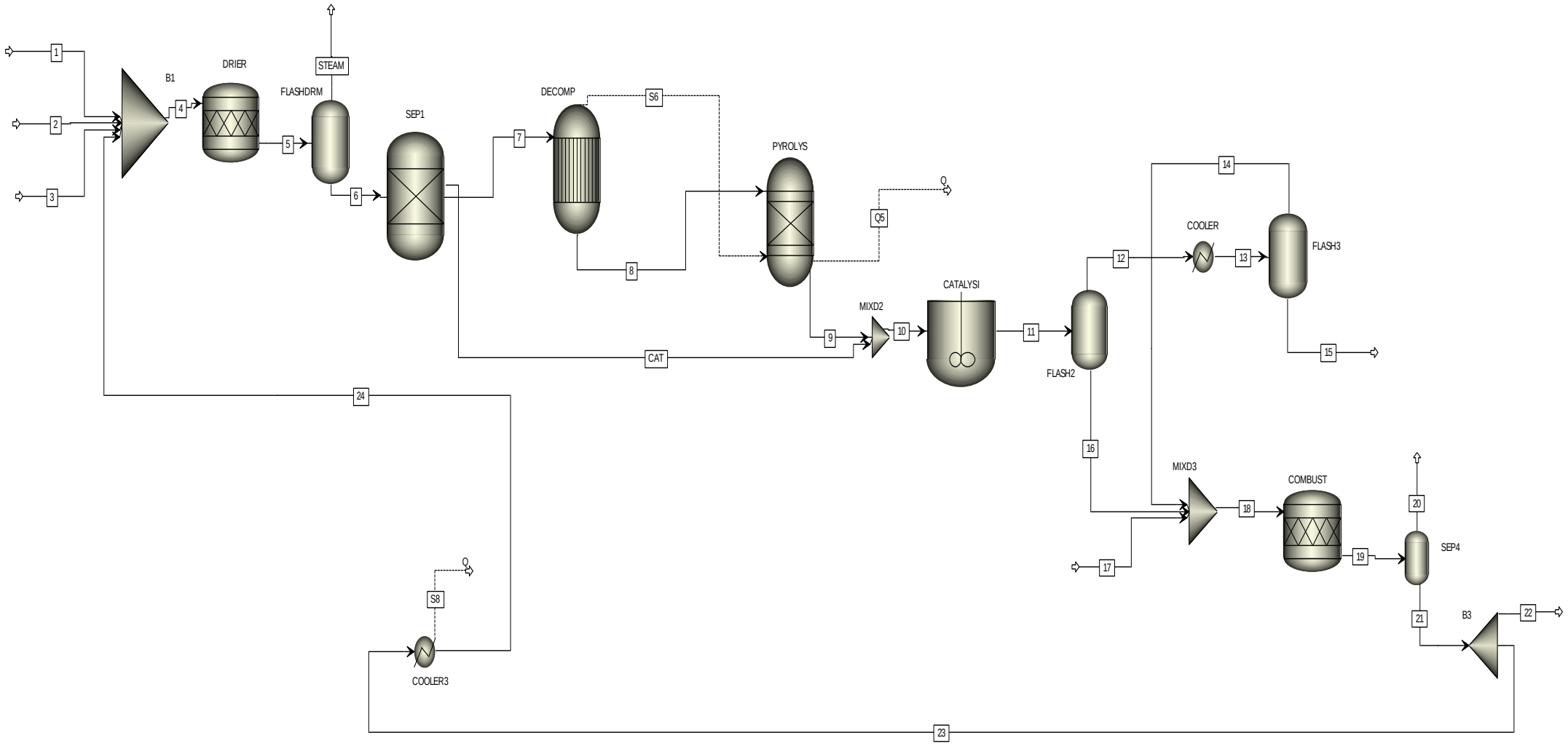

Figure 32Catalytic pyrolysis of lignin into a crude phenolic mixture using zeolite catalyst

Stream	1	2	3	4	5	6	7	8	9	10
Mass Flow kg/hr										
LIGNIN	5525.0	0.0	0.0	5525.0	4998.9	4998.9	0.0	4998.9	0.0	0.0
WATER	0.0	2762.0	0.0	2762.0	526.1	0.0	526.1	0.0	499.9	0.0
CATALYST	0.0	0.0	553.0	553.0	553.0	553.0	0.0	0.0	0.0	553.0
CARBON	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2298.5	0.0
HYDROGEN	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	295.1	0.0
OXYGEN	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1877.9	0.0
SULPHUR	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.9	0.0
ASH	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	19.8	0.0
CARBON DIOXIDE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NITROGEN	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.7	0.0
METHANE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
PHENOL	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
P-CRESOL	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
STEAM	0.0	0.0	0.0	0.0	2762.0	0.0	2762.0	0.0	0.0	0.0
GUAIACOL	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
O-CRESOL	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SYRIGNOL	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CATECHOL	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
EUGENOL	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
DIMETHXOYPHENOL	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SYRINGAHYDE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ACETOVANNILONE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
VINYL GUAIACOL	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
PYRAGALLOL	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
BENZENEDIOL	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ACETOSYRINGONE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
OLIGOMERS	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Flow kg/hr	5525.0	2762.0	553.0	8840.0	8840.0	5551.9	3288.1	4998.9	4998.9	553.0
Temperature C	25.0	25.0	25.0	25.0	100.0	100.0	100.0	100.0	550.0	100.0
Pressure bar	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Enthalpy MW	-20.8	-12.2	-5.0	-12.2	-12.1	-5.1	-12.1	-18.3	-0.8	-5.0
Entropy J/kg-K		-9055.6	-3074.8	-9055.6	-1836.4	-2885.9	-1836.4	1234	2896.1	-2885.9

Stream	11	12	13	15	14	16	17	18	19	20
Mass Flow kg/hr										
LIGNIN	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
WATER	521.0	521.0	523.4	523.4	60.8	523.4	462.6	0.0	60.8	591.3
CATALYST	0.0	553.0	553.0	0.0	0.0	0.0	0.0	553.0	553.0	553.0
CARBON	1036.2	1036.2	1037.8	0.0	0.0	0.0	0.0	1037.8	1037.8	0.0
HYDROGEN	146.4	146.4	131.6	131.6	131.6	131.6	0.0	0.0	131.6	131.6
OXYGEN	1596.4	1596.4	1596.4	1596.4	1595.7	1596.4	0.7	0.0	6845.7	3129.7
SULPHUR	0.9	0.9	0.9	0.9	0.0	0.9	0.9	0.0	0.0	0.0
ASH	19.8	19.8	19.8	0.0	0.0	0.0	0.0	19.8	19.8	19.8
CARBON	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4465.1
NITROGEN	6.2	6.2	6.2	6.2	6.2	6.2	0.0	0.0	19756.3	19756.3
METHANE	182.1	182.1	232.5	232.5	232.2	232.5	0.2	0.0	232.2	0.0
PHENOL	8.8	8.8	340.4	340.4	1.6	340.4	338.8	0.0	1.6	0.0
P-CRESOL	29.6	29.6	29.6	29.6	0.0	29.6	29.5	0.0	0.0	0.0
STEAM	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
GUAIACOL	16.2	16.2	10.4	10.4	0.0	10.4	10.4	0.0	0.0	0.0
O-CRESOL	2.9	2.9	2.9	2.9	0.0	2.9	2.9	0.0	0.0	0.0
SYRINGOL	20.0	20.0	20.0	20.0	0.0	20.0	20.0	0.0	0.0	0.0
CATECHOL	12.7	12.7	1.1	1.1	0.0	1.1	1.1	0.0	0.0	0.0
EUGENOL	9.9	9.9	9.9	9.9	0.0	9.9	9.9	0.0	0.0	0.0
DIMETHOXYPHENOL	19.3	19.3	2.9	2.9	0.0	2.9	2.9	0.0	0.0	0.0
SYRINGAHYDE	61.2	61.2	61.2	61.2	0.0	61.2	61.2	0.0	0.0	0.0
ACETOTOVANNILONE	6.3	6.3	6.3	6.3	0.0	6.3	6.3	0.0	0.0	0.0
VINYL GUAIACOL	40.2	40.2	40.2	40.2	0.0	40.2	40.2	0.0	0.0	0.0
SYRINGOL	38.7	38.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
BENZENEDIOL	35.9	35.9	35.9	35.9	0.0	35.9	35.9	0.0	0.0	0.0
ACETOSYRINGONE	35.3	35.3	35.3	35.3	0.0	35.3	35.3	0.0	0.0	0.0
OLIGOMERS	1060.4	1060.4	391.1	391.1	0.0	391.1	391.1	0.0	0.0	0.0
Total Flow kg/hr	4978.3	5531.3	5511.5	3900.9	2035.6	3900.9	1865.3	1610.6	28646.2	28646.8
Temperature C	550.0	501.5	550.0	550.0	25.0	25.0	25.0	550.0	73.0	850.0
Pressure bar	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Enthalpy MW	-1.4	-1.6	-1.6	-1.6	-0.5	-0.3	-2.8	0.0	-0.1	-5.7
Entropy J/kg-K	742.6	601.4	841.8	841.7	-64.7	-2606.6	-5345.2	8829.2	374.9	1793.3

Stream	21	22	23	24	25	26
Mass Flow kg/hr						
LIGNIN	0.0	0.0	0.0	0.0	0.0	0.0
WATER	591.3	0.0	0.0	0.0	0.0	0.0
CATALYST	0.0	0.0	1105.0	0.0	1105.0	1105.0
CARBON	0.0	0.0	0.0	0.0	0.0	0.0
HYDROGEN	131.6	0.0	0.0	0.0	0.0	0.0
OXYGEN	3129.7	5250.0	0.0	0.0	0.0	0.0
SULPHUR	0.0	0.0	0.0	0.0	0.0	0.0
ASH	0.0	0.0	19.8	0.0	19.8	19.8
CARBON DIOXIDE	4465.1	0.0	0.0	0.0	0.0	0.0
NITROGEN	19756.3	19750.0	0.0	0.0	0.0	0.0
METHANE	0.0	0.0	0.0	0.0	0.0	0.0
PHENOL	0.0	0.0	0.0	0.0	0.0	0.0
P-CRESOL	0.0	0.0	0.0	0.0	0.0	0.0
STEAM	0.0	0.0	0.0	0.0	0.0	0.0
SYRINGOL	0.0	0.0	0.0	0.0	0.0	0.0
CATECHOL	0.0	0.0	0.0	0.0	0.0	0.0
O-CRESOL	0.0	0.0	0.0	0.0	0.0	0.0
EUGENOL	0.0	0.0	0.0	0.0	0.0	0.0
DIMETHOXYPHENOL	0.0	0.0	0.0	0.0	0.0	0.0
SYRINGAHYDE	0.0	0.0	0.0	0.0	0.0	0.0
ACETOVANNILONE	0.0	0.0	0.0	0.0	0.0	0.0
VINYL GUAIACOL	0.0	0.0	0.0	0.0	0.0	0.0
PYROGALLOL	0.0	0.0	0.0	0.0	0.0	0.0
BENZENDIOL	0.0	0.0	0.0	0.0	0.0	0.0
ACETOSYRINGONE	0.0	0.0	0.0	0.0	0.0	0.0
OLIGOMERS	0.0	0.0	0.0	0.0	0.0	0.0
Total Flow kg/hr	28074.0	25000.0	1124.8	0.0	1124.8	1124.8
Temperature C	850.0	25.0	850.0	850.0	850.0	25.0
Pressure bar	1.0	1.0	1.0	1.0	1.0	1.0
Enthalpy MW	-1.2	-1.3	-0.9	-0.5	-0.9	-0.5
Entropy J/kg-K	987	546	687	657	987	576

A3 Fractionation of crude phenolic mixture produced by catalytic pyrolysis of lignin using sodium hydroxide catalyst

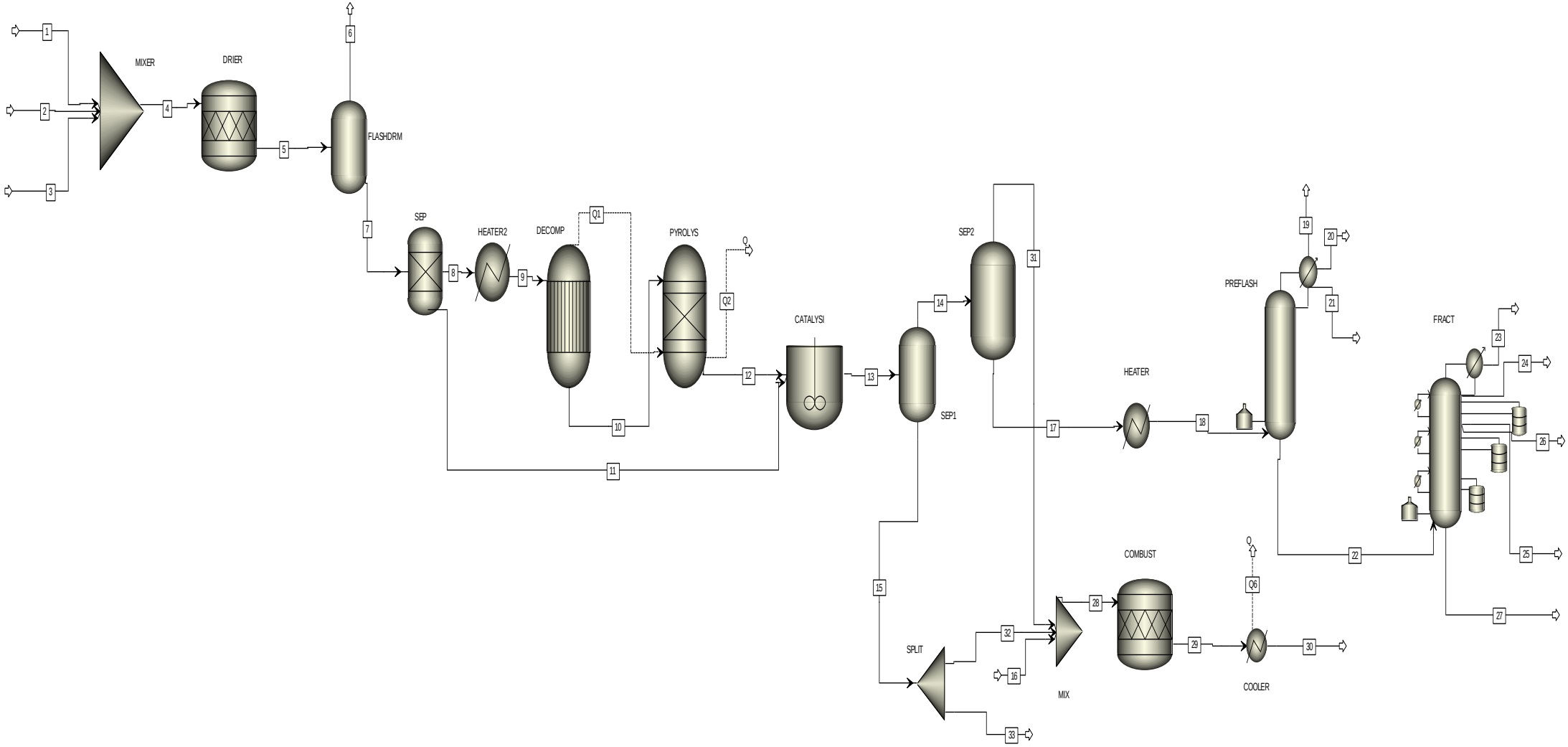

Figure 33 Fractionation of a crude phenolic mixture produced by catalytic (NaOH) pyrolysis of lignin

Stream	1	2	3	4	5	6	7	8	9	10
Mass Flow kg/hr										
LIGNIN	5525	0	0	5525	4998.9	0	4998.9	4998.9	4998.9	0
WATER	0	0	55.3	55.3	526.1	526.1	0	0	0	499.9
CATALYST	0	1234	0	1234	1234	0	1234	0	0	0
CARBON	0	0	0	0	0	0	0	0	0	2298.5
HYDROGEN	0	0	0	0	0	0	0	0	0	295.1
OXYGEN	0	0	0	0	0	0	0	0	0	1877.9
SULPHUR	0	0	0	0	0	0	0	0	0	0.9
ASH	0	0	0	0	0	0	0	0	0	19.8
CARBON DIOXIDE	0	0	0	0	0	0	0	0	0	0
NITROGEN	0	0	0	0	0	0	0	0	0	6.7
METHANE	0	0	0	0	0	0	0	0	0	0
PHENOL	0	0	0	0	0	0	0	0	0	0
P- CRESOL	0	0	0	0	0	0	0	0	0	0
STEAM	0	0	0	0	55.3	55.3	0	0	0	0
EUGENOL	0	0	0	0	0	0	0	0	0	0
GUAIACOL	0	0	0	0	0	0	0	0	0	0
O-CRESOL	0	0	0	0	0	0	0	0	0	0
GUAIACOL	0	0	0	0	0	0	0	0	0	0
METHY-PHENOL	0	0	0	0	0	0	0	0	0	0
SYRINGOL	0	0	0	0	0	0	0	0	0	0
ETHYLPHENOL	0	0	0	0	0	0	0	0	0	0
ACETOSYRINGONE	0	0	0	0	0	0	0	0	0	0
BENZOFURAN	0	0	0	0	0	0	0	0	0	0
SYRINGALDEHYDE	0	0	0	0	0	0	0	0	0	0
ACETOVANNILONE	0	0	0	0	0	0	0	0	0	0
OLIGOMERS	0	0	0	0	0	0	0	0	0	0
Total Flow kg/hr	5525	1234	55.3	6814.3	6814.2	581.4	6232.9	4998.9	4998.9	4998.9
Temperature C	25	25	25	25	100	100	100	100	550	550
Pressure bar	1	1	1	1	1	1	1	1	1	1
Enthalpy MW	-20.8	-5.6	-0.2	-0.2	-2.1	-2.1	-18.3	-18.3	-16.9	-0.8
Entropy kJ/kg-K		-3.1	-9.1	-9.1	-1.9	-1.9	-5.5	2.2	2.3	2.9

Stream	11	12	13	14	15	16	17	18	19	20
Mass Flow kg/hr										
LIGNIN	0	0	0	0	0	0	0	0	0	0
WATER	0	914.6	914.6	914.6	0	0	68.5	68.5	0.1	66.1
CATALYST	1234	0	1234	0	1234	0	0	0	0	0
CARBON	0	1276.2	1276.2	0	1276.2	0	0	0	0	0
HYDROGEN	0	128.8	128.8	128.8	0	0	0	0	0	0
OXYGEN	0	1295.5	1295.5	1295.5	0	2300	0.1	0.1	0.1	0
SULPHUR	0	0.9	0.9	0.9	0	0	0.9	0.9	0	0
ASH	0	19.8	19.8	0	19.8	0	0	0	0	0
CARBON DIOXIDE	0	0	0	0	0	0	0	0	0	0
NITROGEN	0	6.2	6.2	6.2	0	0	0	0	0	0
METHANE	0	155.2	155.2	155.2	0	0	0	0	0	0
PHENOL	0	8.1	8.1	8.1	0	0	5	5	0	0
P- CRESOL	0	0.4	0.4	0.4	0	0	0.3	0.3	0	0
STEAM	0	0	0	0	0	0	0	0	0	0
EUGENOL	0	11.7	11.7	11.7	0	0	11.7	11.7	0	0
GUAIACOL	0	20	20	20	0	0	17.3	17.3	0	0
O-CRESOL	0	12.5	12.5	12.5	0	0	12.4	12.4	0	0
GUAIACOL	0	18.6	18.6	18.6	0	0	16.3	16.3	0	0
METHY-PHENOL	0	10.6	10.6	10.6	0	0	10.5	10.5	0	0
SYRINGOL	0	6.7	6.7	6.7	0	0	6.7	6.7	0	0
ETHYLPHENOL	0	28.7	28.7	28.7	0	0	26.1	26.1	0	0
ACETOSYRINGONE	0	40.2	40.2	40.2	0	0	40.1	40.1	0	0
BENZOFURAN	0	38.7	38.7	38.7	0	0	38.7	38.7	0	0
SYRINGALDEHYDE	0	35.9	35.9	35.9	0	0	35.9	35.9	0	0
ACETOVANNILONE	0	35.3	35.3	35.3	0	0	35.3	35.3	0	0
OLIGOMERS	0	857.1	857.1	857.1	0	0	857.1	857.1	0	0
Total Flow kg/hr	1234	4986.4	6220.4	3690.4	2530	2300	1246.5	1246.5	0.3	66.1
Temperature C	100	550	550	550	550	25	90	200	100	100
Pressure bar	1	1	1	1	1	1	1	1	1	1
Enthalpy MW	-5.6	-2.9	-2.9	-2.9	-5.2	-4.5	-0.9	-0.7	0	-0.3
Entropy J/kg-K	-2.9	0.7	0.7	0.7	-0.3	0.2	-4.2	-3.3	-0.7	-8.1

Stream	21	22	23	24	25	26	27	28	29	30
Mass Flow kg/hr										
LIGNIN	0	0	0	0	0	0	0	0	0	0
WATER	2.3	0	0	0	0	0	0	846.1	2345.9	2345.9
CATALYST	0	0	0	0	0	0	0	493.6	493.6	493.6
CARBON	0	0	0	0	0	0	0	510.5	0	0
HYDROGEN	0	0	0	0	0	0	0	128.8	0	0
OXYGEN	0	0	0	0	0	0	0	2300	2300	2300
SULPHUR	0	0.9	0	0	0	0	0.9	0	0	0
ASH	0	0	0	0	0	0	0	7.9	7.9	7.9
CARBON DIOXIDE	0	0	0	0	0	0	0	0	2296.6	2296.6
NITROGEN	0	0	0	0	0	0	0	6.2	6.2	6.2
METHANE	0	0	0	0	0	0	0	155.1	0	0
PHENOL	5	0	0	0	0	0	0	3.1	3.1	3.1
P- CRESOL	0.3	0	0	0	0	0	0	0.1	0.1	0.1
STEAM	0	0	0	0	0	0	0	0	0	0
EUGENOL	0	11.7	0	4	2.2	0.6	4.9	0	0	0
GUAIACOL	1.5	0	0	0	0	0	0	0.5	0.5	0.5
O-CRESOL	15.9	1.4	0	0.8	0.4	0	0.2	2.7	2.7	2.7
GUAIACOL	0	12.4	0	5.4	2.7	0.4	3.8	0.1	0.1	0.1
METHY-PHENOL	5.5	10.8	0	5.4	2.6	0.3	2.5	2.3	2.3	2.3
SYRINGOL	0	10.5	0	3.2	1.9	0.6	4.9	0	0	0
ETHYLPHENOL	0	6.7	0	0	0.2	0.7	5.9	0	0	0
ACETOSYRINGONE	10.7	15.4	0	8	3.7	0.4	3.2	2.6	2.6	2.6
BENZOFURAN	0	38.7	0	5.8	6.8	2.7	23.3	0	0	0
SYRINGALDEHYDE	0	35.9	0	0	0	0	35.9	0	0	0
ACETOVANNILONE	0	35.3	0	10	6.3	2	17	0.1	0.1	0.1
OLIGOMERS	0	857.1	0	0.2	52.4	86	718.5	0	0	0
Total Flow kg/hr	41.3	1138.8	0	75	100	100	875.6	2300	8466	8757
Temperature C	100	324.9	324	269.3	337.3	339.7	341.6	25.5	900	100
Pressure bar	1	1	1	1	1	1	1	1	1	1
Enthalpy MW	0	-0.4	-0.3	0	0	0	-0.2	-3.1	56.3	30
Entropy J/kg-K	-3.8	-2.8	-2.3	-2.8	-2.1	-2.8	-2.8	0.01	1.4	0.2

Stream	31	32	33
Mass Flow kg/hr			
LIGNIN	0	0	0
WATER	846.1	0	0
CATALYST	0	493.6	740.4
CARBON	0	510.5	765.7
HYDROGEN	128.8	0	0
OXYGEN	1295.3	0	0
SULPHUR	0	0	0
ASH	0	7.9	11.9
CARBON DIOXIDE	0	0	0
NITROGEN	6.2	0	0
METHANE	155.1	0	0
PHENOL	3.1	0	0
P- CRESOL	0.1	0	0
STEAM	0	0	0
EUGENOL	0	0	0
GUAIACOL	0.5	0	0
O-CRESOL	2.7	0	0
GUAIACOL	0.1	0	0
METHY-PHENOL	2.3	0	0
SYRINGOL	0	0	0
ETHYLPHENOL	0	0	0
ACETOSYRINGONE	2.6	0	0
BENZOFURAN	0	0	0
SYRINGALDEHYDE	0	0	0
ACETOVANNILONE	0.1	0	0
OLIGOMERS	0	0	0
Total Flow kg/hr	2443.9	1012	1518
Temperature C	90	550	550
Pressure bar	1	1	1
Enthalpy MW	-3.3	-2.1	-3.1
Entropy J/kg-K	-0.1	-0.3	-0.3

A4 Fractionation of crude phenolic mixture produced by catalytic pyrolysis of lignin using zeolite catalyst

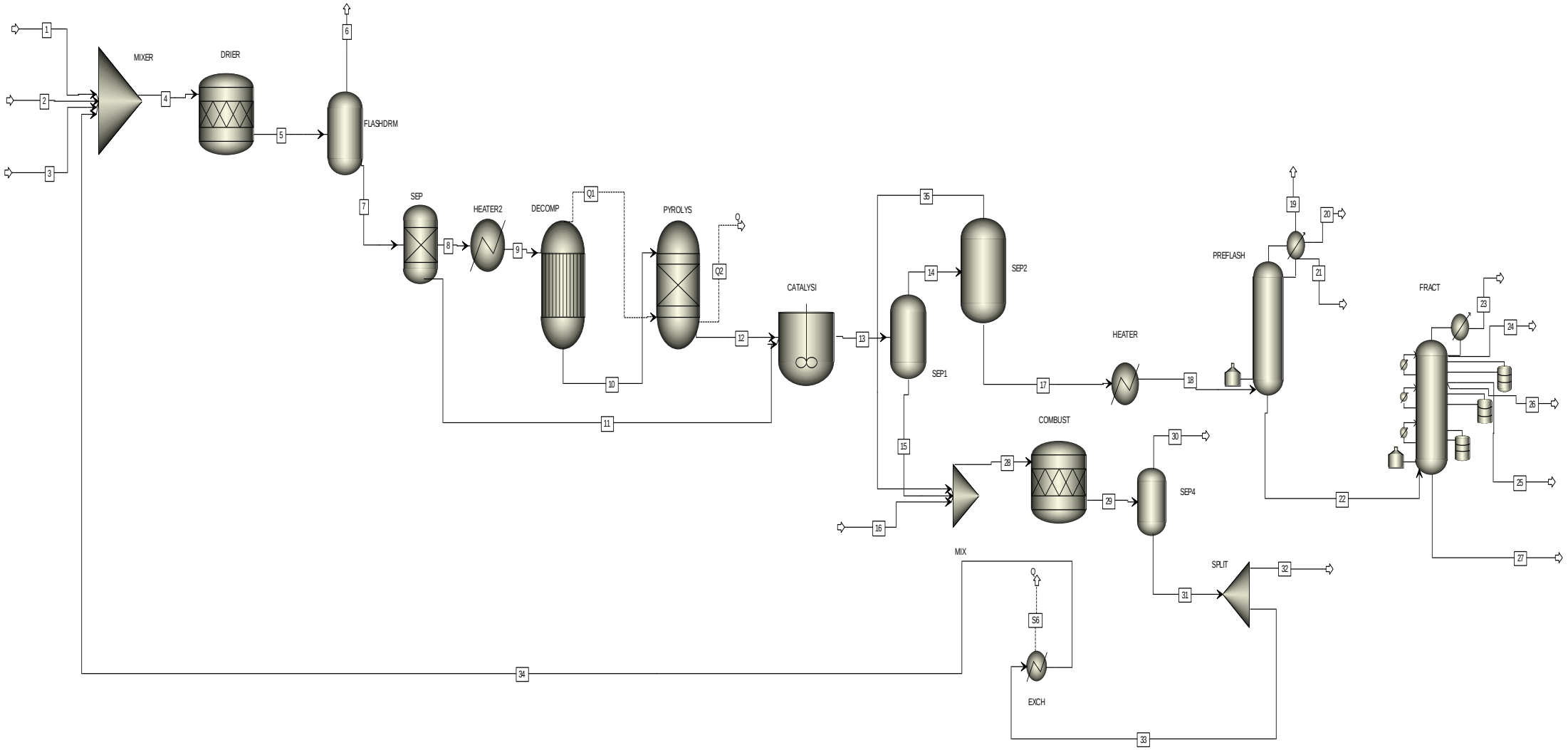

Figure 34 Fractionation of crude phenolic mixture produced by catalytic (Zeolite) pyrolysis of lignin

Stream	1	2	3	4	5	6	7	8	9	10
Mass Flow kg/hr										
LIGNIN	5525	0	0	5525	4998.9	0	4998.9	4998.9	4998.9	0
WATER	0	0	55.25	55.25	526.1	526.1	0	0	0	499.89
CATALYST	0	1234	0	1234	1234	0	1234	0	0	0
CARBON	0	0	0	0	0	0	0	0	0	2298.54
HYDROGEN	0	0	0	0	0	0	0	0	0	295.13
OXYGEN	0	0	0	0	0	0	0	0	0	1877.89
SULPHUR	0	0	0	0	0	0	0	0	0	0.9
ASH	0	0	0	0	0	0	0	0	0	19.8
CARBON	0	0	0	0	0	0	0	0	0	0
NITROGEN	0	0	0	0	0	0	0	0	0	6.75
METHANE	0	0	0	0	0	0	0	0	0	0
PHENOL	0	0	0	0	0	0	0	0	0	0
P-CRESOL	0	0	0	0	0	0	0	0	0	0
STEAM	0	0	0	0	0	0	0	0	0	0
GUAIACOL	0	0	0	0	0	0	0	0	0	0
O-CRESOL	0	0	0	0	55.25	55.25	0	0	0	0
SYRINGOL	0	0	0	0	0	0	0	0	0	0
CATECHOL	0	0	0	0	0	0	0	0	0	0
EUGENOL	0	0	0	0	0	0	0	0	0	0
DIMETHOXYPHENOL	0	0	0	0	0	0	0	0	0	0
SYRINGAHYDE	0	0	0	0	0	0	0	0	0	0
ACETOTOVANNILONE	0	0	0	0	0	0	0	0	0	0
VINYL GUAIACOL	0	0	0	0	0	0	0	0	0	0
PROGALLOL	0	0	0	0	0	0	0	0	0	0
BENZENEDIOL	0	0	0	0	0	0	0	0	0	0
ACETOSYRINGONE	0	0	0	0	0	0	0	0	0	0
OLIGOMERS	0	0	0	0	0	0	0	0	0	0
Total Flow kg/hr	5525	1234	55.25	6814.25	6814.25	581.35	6232.9	4998.9	4998.9	4998.9
Temperature C			25	25	100	100				550
Pressure bar	1	1	1	1	1	1	1	1	1	1
Enthalpy MW	-20.77	-5.63	-0.24	-5.99	-27.14	-2.14	-23.84	-18.28	-16.9	-1.1
Entropy J/kg-K		-3.07	-9.06	-11.06	-3.89	-1.89	-2.89	-3.45	2.34	3.9

Stream	11	12	13	14	15	16	17	18	19	20
Mass Flow kg/hr										
LIGNIN	0	0	0	0	0	0	0	0	0	0
WATER	0	914.62	914.62	914.62	0	0	90.68	90.68	0.15	88.17
CATALYST	1234	0	1234	0	1234	0	0	0	0	0
CARBON	0	1061.09	1061.09	0	1061.09	0	0	0	0	0
HYDROGEN	0	104.68	104.68	104.68	0	0	0	0	0	0
OXYGEN	0	1252.08	1252.08	1252.08	0	4566	0.17	0.17	0.17	0
SULPHUR	0	0.9	0.9	0.9	0	0	0.9	0.9	0	0
ASH	0	19.8	19.8	0	19.8	0	0	0	0	0
CARBON	0	0	0	0	0	0	0	0	0	0
NITROGEN	0	6.25	6.25	6.25	0	0	0	0	0	0
METHANE	0	182.1	182.1	182.1	0	0	0.04	0.04	0.04	0
PHENOL	0	8.77	8.77	8.77	0	0	6.01	6.01	0.01	0
P-CRESOL	0	0	0	0	0	0	0	0	0	0
STEAM	0	0.05	0.05	0.05	0	0	0.05	0.05	0	0
GUAIACOL	0	16.23	16.23	16.23	0	0	16.18	16.18	0	0
O-CRESOL	0	20.02	20.02	20.02	0	0	17.95	17.95	0.01	0
SYRINGOL	0	12.72	12.72	12.72	0	0	12.62	12.62	0	0
CATECHOL	0	19.28	19.28	19.28	0	0	18.87	18.87	0	0
EUGENOL	0	22.14	22.14	22.14	0	0	22.07	22.07	0	0
DIMETHOXYPHENOL	0	6.33	6.33	6.33	0	0	6.33	6.33	0	0
SYRINGAHYDE	0	28.74	28.74	28.74	0	0	26.74	26.74	0	0
ACETOVANNILONE	0	40.22	40.22	40.22	0	0	40.16	40.16	0	0
VINYL GUAIACOL	0	38.74	38.74	38.74	0	0	38.71	38.71	0	0
SYRINGOL	0	35.91	35.91	35.91	0	0	35.91	35.91	0	0
BENZENEDIOL	0	35.33	35.33	35.33	0	0	35.28	35.28	0	0
ACETOSYRINGONE	0	35.33	35.33	35.33	0	0	35.28	35.28	0	0
OLIGOMERS	0	1060.43	1060.43	1060.43	0	0	1060.43	1060.43	0	0
Total Flow kg/hr	1234	4983.95	6217.95	3903.07	2314.88	4566	1523.79	1523.79	0.38	88.17
Temperature C		550	550	550		25	90	200	100	100
Pressure bar	1	1	1	1	1	1	1	1	1	1
Enthalpy MW	-5.61	-2.99	-5.76	-2.99	-5.27	0	-1.08	-0.92	0	-0.38
Entropy J/kg-K	-2.89	1.46	0.96	0.46	-0.43	0	-4.26	-3.33	-0.84	-8.12

Stream	21	22	23	24	25	26	27	28	29	30
Mass Flow kg/hr										
LIGNIN	0	0	0	0	0	0	0	0	0	0
WATER	2.36	0	0	0	0	0	0	823.94	2169.27	2169.27
CATALYST	0	0	0	0	0	0	0	1234	1234	0
CARBON	0	0	0	0	0	0	0	1061.09	0	0
HYDROGEN	0	0	0	0	0	0	0	104.68	0	0
OXYGEN	0.01	0	0	0	0	0	0	4566	4566	4566
SULPHUR	0	0.9	0	0	0	0	0.9	0	0	0
ASH	0	0	0	0	0	0	0	19.8	19.8	0
CARBON	0	0	0	0	0	0	0	0	4388.91	4388.91
NITROGEN	0	0	0	0	0	0	0	6.25	6.25	6.25
METHANE	0	0	0	0	0	0	0	182.06	0	0
PHENOL	5.99	0	0	0	0	0	0	2.76	2.76	2.76
P-CRESOL	0.54	0	0	0	0	0	0	0.11	0.11	0.11
STEAM	0	0	0	0	0	0	0	0	0	0
GUAIACOL	0	0.05	0	0	0.01	0	0.03	0	0	0
O-CRESOL	0	16.18	0	4.55	2.95	0.71	7.96	0.05	0.05	0.05
SYRINGOL	16.32	1.62	0	0.86	0.41	0.03	0.32	2.07	2.07	2.07
CATECHOL	0	12.62	0	4.91	2.62	0.42	4.68	0.09	0.09	0.09
EUGENOL	2.85	6.16	0	2.85	1.41	0.15	1.75	0.93	0.93	0.93
DIMETHOXYPHENOL	0.05	18.82	0	7.81	4.01	0.57	6.43	0.41	0.41	0.41
SYRINGAHYDE	0	22.07	0	5.46	3.79	1.06	11.77	0.07	0.07	0.07
ACETOVANNILONE	10.37	16.37	0	7.87	3.85	0.38	4.27	2	2	2
VINYL GUAIACOL	0	38.71	0	2.72	7.65	2.33	26	0.03	0.03	0.03
SYRINGOL	0	35.91	0	0	0	0	35.91	0	0	0
BENZENEDIOL	0	35.28	0	7.61	6.36	1.75	19.56	0.05	0.05	0.05
ACETOSYRINGONE	0	35.28	0	9.35	6.54	1.59	17.8	0.05	0.05	0.05
OLIGOMERS	0	1060.43	0	0.02	41.9	85.37	933.14	0	0	0
Total Flow kg/hr	41.62	1393.61	0	72.17	100	100	13390	6754.26	12357	11123
Temperature C	100	323		265.43	330.58	336.64	338.09	25.89	900	850
Pressure bar	1	1	1	1	1	1	1	1	1	1
Enthalpy MW	-0.02	-0.45	0.34	-0.05	-0.03	-0.03	-0.32	-8.34	8.87	7.99
Entropy J/kg-K	-3.85	-2.84	-3.4	-2.82	-2.06	-2.84	-2.79	-1.66	2.39	1.34

Stream	31	32	33	34	35
Mass Flow kg/hr					
LIGNIN	0	0	0	0	0
WATER	0	0	0	0	823.94
CATALYST	1234	493.6	740.4	740.4	0
CARBON	0	0	0	0	0
HYDROGEN	0	0	0	0	104.68
OXYGEN	0	0	0	0	1251.91
SULPHUR	0	0	0	0	0
ASH	19.8	7.92	11.88	11.88	0
CARBON	0	0	0	0	0
NITROGEN	0	0	0	0	6.25
METHANE	0	0	0	0	182.06
PHENOL	0	0	0	0	2.76
P-CRESOL	0	0	0	0	0.11
STEAM	0	0	0	0	0
GUAIACOL	0	0	0	0	0.05
O-CRESOL	0	0	0	0	0.58
SYRINGOL	0	0	0	0	2.07
CATECHOL	0	0	0	0	0.09
EUGENOL	0	0	0	0	0.32
DIMETHOXYPHENOL	0	0	0	0	0.93
SYRINGAHYDE	0	0	0	0	0.41
ACETOVANNILONE	0	0	0	0	0.07
VINYL GUAIACOL	0	0	0	0	0.01
SYRINGOL	0	0	0	0	0.07
BENZENEDIOL	0	0	0	0	0.03
ACETOSYRINGONE	0	0	0	0	0.05
OLIGOMERS	0	0	0	0	0.05
Total Flow kg/hr	1253.8	501.52	752.28	752.28	2379.29
Temperature C		0	0	0	90
Pressure bar	1	0	0	0	1
Enthalpy MW	3.66	8.87	3.87	-4.99	-6.87
Entropy J/kg-K	-1.33	1	1	1	-0.19

A5 CAPITAL COST BREAK DOWN OF THE PHENOLIC COMPOUND PRODUCTION SCENARIOS

Table 20 Scenario 1: Catalytic pyrolysis of lignin into a crude phenolic mixture using sodium hydroxide catalyst

Process Area				Purchased Cost		Installed Cost
Area 000: pyrolysis				-	$	23 117 850
Area Pyrolysis auxiliary				-	$	1 790 788
Drier					$	20 000
Area 800: Storage (5 % of ISBL)				-	$	1 245 432
Area 900: Utilities (6.5% of ISBL)				-	$	1 619 061
Totals				**$ -**	**$**	**27 773 131**
Warehouse	4.0%	of ISBL			$	996 346
Site Development	9.0%	of ISBL			$	2 241 777
Additional Piping	4.5%	of ISBL			$	1 120 889
Total Direct Costs (TDC)					**$**	**32 132 143**
Prorateable Expenses	10.0%	of TDC			$	3 213 214
Field Expenses	10.0%	of TDC			$	3 213 214
Home Office & Construction Fee	20.0%	of TDC			$	6 426 429
Project Contingency	10.0%	of TDC			$	3 213 214
Other Costs (Start-Up, Permits, etc.)	10.0%	of TDC			$	3 213 214
Total Indirect Costs					**$**	**19 279 286**
Fixed Capital Investment (FCI)					**$**	**51 411 429**
South Africa Location Factor (LF)					1.0	
Corrected Fixed Capital Investment (FCI)					**$**	**51 411 429**
Working Capital			5.0%	of FCI	$	2 570 571
Land					$	-
Corrected Total Capital Investment (TCI)					**$**	**53 982 000**

Table 21 Scenario 2: Catalytic pyrolysis of lignin into a crude phenolic mixture using zeolite catalyst

Process Area			Purchased Cost		Installed Cost
Area 000: pyrolysis			$ -	$	23 117 850
Area Pyrolysis auxiliary			$ -	$	1 790 788
Cost of catalyst to fill reactor.			$ -	$	3 030 000
Drier			$	$	20 000
Area 800: Storage (5 % of ISBL)			$ -	$	1 396 932
Area 900: Utilities (6.5% of ISBL)			$ -	$	1 816 011
Totals			**$ -**	**$**	**31 151 581**
Warehouse	4.0%	of ISBL		$	1 117 546
Site Development	9.0%	of ISBL		$	2 514 477
Additional Piping	4.5%	of ISBL		$	1 257 239
Total Direct Costs (TDC)				**$**	**36 040 843**
Prorateable Expenses	10.0%	of TDC		$	3 604 084
Field Expenses	10.0%	of TDC		$	3 604 084
Home Office & Construction Fee	20.0%	of TDC		$	7 208 169
Project Contingency	10.0%	of TDC		$	3 604 084
Other Costs (Start-Up, Permits, etc.)	10.0%	of TDC		$	3 604 084
Total Indirect Costs				**$**	**21 624 506**
Fixed Capital Investment (FCI)				**$**	**57 665 349**
South Africa Location Factor (LF)					1.0
Corrected Fixed Capital Investment (FCI)				**$**	**57 665 349**
Working Capital	5.0%	of FCI		$	2 883 267
Land				$	-
Corrected Total Capital Investment (TCI)				**$**	**60 548 616**

Table 22 Scenario 3: Fractionation of a crude phenolic mixture produced from catalytic (NaOH) pyrolysis of lignin

Process Area			Purchased Cost	Installed Cost
Area 000: pyrolysis			$ -	$ 23 117 850
Area Pyrolysis auxiliary			$ -	$ 1 790 788
Drier			$	$ 20 000
Purification			$ -	$ 1 096 600
Area 800: Storage (5 % of ISBL)			$ -	$ 1 301 262
Area 900: Utilities (6.5% of ISBL)			$ -	$ 1 691 640
Totals			**$ -**	**$ 29 018 140**
Warehouse	4.0%	of ISBL		$ 1 041 010
Site Development	9.0%	of ISBL		$ 2 342 271
Additional Piping	4.5%	of ISBL		$ 1 171 136
Total Direct Costs (TDC)				**$ 33 572 557**
Prorateable Expenses	10.0%	of TDC		$ 3 357 256
Field Expenses	10.0%	of TDC		$ 3 357 256
Home Office & Construction Fee	20.0%	of TDC		$ 6 714 511
Project Contingency	10.0%	of TDC		$ 3 357 256
Other Costs (Start-Up, Permits, etc.)	10.0%	of TDC		$ 3 357 256
Total Indirect Costs				**$ 20 143 534**
Fixed Capital Investment (FCI)				**$ 53 716 091**
South Africa Location Factor (LF)				1.0
Corrected Fixed Capital Investment (FCI)				**$ 53 716 091**
Working Capital	5.0%	of FCI		$ 2 685 805
Land				$ -
Corrected Total Capital Investment (TCI)				**$ 56 401 896**

Table 23 Scenario 4: Fractionation of a crude phenolic mixture produced from catalytic (Zeolite) pyrolysis of lignin

Process Area			Purchased Cost		Installed Cost	
Area 000: pyrolysis			$ -	$	23 117 850	
Area Pyrolysis auxiliary			$ -	$	1 790 788	
Purification			$ -	$	1 096 600	
Catalyst loading			$ -	$	3 030 000	
Drier			$ -	$	20 000	
Area 800: Storage (5 % of ISBL)			$ -	$	1 452 762	
Area 900: Utilities (6.5% of ISBL)			$ -	$	1 888 590	
Totals			**$ -**	**$**	**32 396 590**	
Warehouse	4.0%	of ISBL		$	1 162 210	
Site Development	9.0%	of ISBL		$	2 614 971	
Additional Piping	4.5%	of ISBL		$	1 307 486	
Total Direct Costs (TDC)				**$**	**37 481 257**	
Prorateable Expenses	10.0%	of TDC		$	3 748 126	
Field Expenses	10.0%	of TDC		$	3 748 126	
Home Office & Construction Fee	20.0%	of TDC		$	7 496 251	
Project Contingency	10.0%	of TDC		$	3 748 126	
Other Costs (Start-Up, Permits, etc.)	10.0%	of TDC		$	3 748 126	
Total Indirect Costs				**$**	**22 488 754**	
Fixed Capital Investment (FCI)				**$**	**59 970 011**	
South Africa Location Factor (LF)						1.0
Corrected Fixed Capital Investment (FCI)				**$**	**59 970 011**	
Working Capital	5.0%	of FCI		$	2 998 501	
Land				$	-	
Corrected Total Capital Investment (TCI)				**$**	**62 968 512**	

A6 OPERATING COST BREAKDOWN OF THE DEVELOPED SCENARIOS

Table 24 Scenario 1: Catalytic pyrolysis of lignin into a crude phenolic mixture using sodium hydroxide catalyst

Raw Material	Stream No.	kg/hr	lb/hr	Quoted Price (cents / ton)	Year of Price Quote	2015 cost $ /ton	MM $ /Year 2015
Feedstock	Lignin	5 525	12 183	2200	2015	22.00	0.79
NaOH Catalyst	CATALYST	1 325.00	2 922		2015	300	2.58
		0.00	-		2015		0.05
Cooling Tower Chemicals	-	0.20	0	200000	1999	2679.55	0.00
Makeup Water	L704	1 000	2 205	20	2004	0.24	0.00
Subtotal							**3.41**
Total Variable Operating Costs							**3.41**

Position	Salary	Year of salary quote	2015 Salary	# Required	Total		MM $ /Year 2015
Plant Manager	147000	2015	172 642	1	172 642		
Plant Engineer	70000	2015	82 211	1	82 211		
Maintenance Tech	40000	2015	46 978	2	93 955		
Lab Technician	40000	2015	46 978	1	46 978		
Shift Supervisor	48000	2015	56 373	2	112 746		
Shift Operators	40000	2015	46 978	7	328 843		
Clerks & Secretaries	36000	2015	42 280	1	42 280		
Total Salaries				16	912 538		**0.91**
Labour Burden (90%)					821 284		**0.82**
Maintenance	3.0%	of ISBL				747 259	0.75
Property Insurance. & Tax	0.7%	of FCI				359 880	0.36
Total Fixed Operating Costs							**2.84**
		ISBL=	$24 908 638				
		FCI=	$51 411 429				
Total Operating Costs							**6.25**

Table 25 Scenario 2: Catalytic pyrolysis of lignin into a crude phenolic mixture using zeolite catalyst

Raw Material	Stream No.	kg/hr		Quoted Price (cents / ton)	2015 cost $ /ton	$/hour	MM $ /Year 2015
Raw Materials							
Feedstock	Lignin	5 525	2200	2015	22.00	121.55	0.79
Zeolite Catalyst	CATALYST	0.01		2015	850	0.00	0.00
Zeolite		275.50	45000	2009	850.00	234.18	1.52
Cooling Tower Chemicals	-	0.20	200000	1999	2679.55	0.54	0.00
Makeup Water	L704	1 000	20	2004	0.24	0.24	0.00
Waste Streams							
Disposal of Ash	L619	19.01	42	2886	2007	33.05	0.63	0.0041
Total Variable Operating Costs							**2.37**

Fixed Operating Costs							
Position	**Salary**	**Year of salary quote**	**2015 Salary**	**# Required**	**Total**		**MM $ /Year 2015**
Plant Manager	147000	2015	172 642	1	172 642		
Plant Engineer	70000	2015	82 211	1	82 211		
Maintenance Tech	40000	2015	46 978	2	93 955		
Lab Technician	40000	2015	46 978	1	46 978		
Shift Supervisor	48000	2015	56 373	2	112 746		
Shift Operators	40000	2015	46 978	7	328 843		
Clerks & Secretaries	36000	2015	42 280	1	42 280		
Labour Burden (90%)					821 284		**0.82**
Other Overhead							
Maintenance	3.0%	of ISBL				838 159	0.84
Property Insur. & Tax	0.7%	of FCI				403 657	0.40
Total Fixed Operating Costs							2.98
				ISBL=	$27 938 638		
				FCI=	$57 665 349		
Total Operating Costs							**5.35**

Table 26 Scenario 3: Fractionation of a crude phenolic mixture produced from catalytic (NaOH) pyrolysis of lignin

Raw Material	Stream No.	kg/hr	lb/hr	Quoted Price (cents / ton)	Year of Price Quote	2015 cost $ /ton	MM $ /Year 2015
Feedstock	Lignin	5 525	12 183	2200	2015	22.00	0.79
NaOH Catalyst	CATALYST	1 325.00	2 922		2015	300	2.58
		0.00	-		2015		0.05
Cooling Tower Chemicals	-	0.20	0	200000	1999	2679.55	0.00
Makeup Water	L704	1 000	2 205	20	2004	0.24	0.00
Subtotal							**3.41**
Total Variable Operating Costs							**3.41**

Position	Salary		Year of salary quote	2015 Salary	# Required	Total		MM $ /Year 2015
Plant Manager	147000		2015	172 642	1	172 642		
Plant Engineer	70000		2015	82 211	1	82 211		
Maintenance Tech	40000		2015	46 978	2	93 955		
Lab Technician	40000		2015	46 978	1	46 978		
Shift Supervisor	48000		2015	56 373	2	112 746		
Shift Operators	40000		2015	46 978	7	328 843		
Clerks & Secretaries	36000		2015	42 280	1	42 280		
Total Salaries					16	912 538		**0.91**
Labour Burden (90%)						821 284		**0.82**
Maintenance	3.0%	of ISBL					747 259	0.75
Property Insurance. & Tax	0.7%	of FCI					359 880	0.36
Total Fixed Operating Costs								**2.84**
			ISBL=	$24 908 638				
			FCI=	$51 411 429				
Total Operating Costs								**6.25**

Table 27 Fractionation of a crude phenolic mixture produced from catalytic (Zeolite) pyrolysis of lignin

Raw Material	Stream No.	kg/hr		Quoted Price (cents / ton)	2015 cost $ /ton	$/hour	MM $ /Year 2015
Raw Materials							
Feedstock	Lignin	5 525	2200	2015	22.00	121.55	0.79
Zeolite Catalyst	CATALYST	0.01		2015	850	0.00	0.00
Zeolite		275.50	45000	2009	850.00	234.18	1.52
Cooling Tower Chemicals	-	0.20	200000	1999	2679.55	0.54	0.00
Makeup Water	L704	1 000	20	2004	0.24	0.24	0.00
Waste Streams							
Disposal of Ash	L619	19.01	42	2886	2007	33.05	0.63	0.0041
Total Variable Operating Costs							**2.37**

Fixed Operating Costs							
Position	**Salary**	**Year of salary quote**	**2015 Salary**	**# Required**	**Total**		**MM $ /Year 2015**
Plant Manager	147000	2015	172 642	1	172 642		
Plant Engineer	70000	2015	82 211	1	82 211		
Maintenance Tech	40000	2015	46 978	2	93 955		
Lab Technician	40000	2015	46 978	1	46 978		
Shift Supervisor	48000	2015	56 373	2	112 746		
Shift Operators	40000	2015	46 978	7	328 843		
Clerks & Secretaries	36000	2015	42 280	1	42 280		
Labour Burden (90%)					821 284		**0.82**
Other Overhead							
Maintenance	3.0%	of ISBL				838 159	0.84
Property Insur. & Tax	0.7%	of FCI				403 657	0.40
Total Fixed Operating Costs							2.98
				ISBL=	$27 938 638		
				FCI=	$57 665 349		
Total Operating Costs							**5.35**